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A NEW CARBON-BOND MECHANISM FOR AIR QUALITY SIMULATION MODELING

by

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A new generalized kinetic mechanism for photochemical smog, which incorporates recent information on the atmospheric reactions of aromatic hydrocarbons, has been developed. The mechanism, labeled the Carbon-Bond Mechanism III (CBM III), is the third lumped-parameter mechanism to be designed in accordance with the carbon-bond reaction concept in which carbon atoms with similar bonding are treated similarly, regardless of the molecules in which they occur. Because of the general nature of the CBM III, it can be used to model the entire atmospheric mix of hydrocarbons and is suitable for use in air quality simulation models. Principal features of CBM III include a separate reaction scheme for ethylene, realistic photochemistry for aromatic hydrocarbons and dicarbonyl compounds, and formation pathways for alkyl nitrates and nitroaromatic compounds. CBM III was tested by comparing the predictions obtained with the mechanism against smog chamber data of multi-component hydrocarbon/NO_x mixtures. In addition to a discussion of the development and testing of the CBM III, information is also provided on the application of the mechanism for urban air quality modeling.

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ABSTRACT

A new generalized kinetic mechanism for photochemical smog, which incorporates recent information on the atmospheric reactions of aromatic hydrocarbons, has been developed. The mechanism, labeled the Carbon-Bond Mechanism III (CBM-III), is the third lumped-parameter mechanism to be designed in accordance with the carbon-bond reaction concept in which carbon atoms with similar bonding are treated similarly, regardless of the molecules in which they occur. The principal feature that distinguishes CBM-III from previous Carbon-Bond Mechanisms is the updated aromatic hydrocarbon chemistry.

Because of the general nature of the CBM-III, it can be used to model the entire atmospheric mix of hydrocarbons and is suitable for use in Air Quality Simulation Models (AQSMs). Principal features of CBM-III include a separate reaction scheme for ethylene; realistic photochemistry for aromatic hydrocarbons and dicarbonyl compounds; and formation pathways for alkyl nitrates and nitroaromatic compounds.

CBM-III was tested by comparing the predictions obtained with the mechanism against smog chamber data of multi-component hydrocarbon/NO_x mixtures obtained in the indoor chamber facility at the University of California, Riverside, and the outdoor chamber facility of the University of North Carolina.

In addition to a discussion of the development and testing of the CBM-III, information is also provided on the application of the mechanism for urban air quality modeling. Instructions are given on how to partition the emission and atmospheric hydrocarbon data into the various carbon-bond groupings that are used in the CBM-III. Calculated bond groupings are given for several types of hydrocarbon data (including data for several specific urban areas).

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LIST OF ABBREVIATIONS

ACO_3	Peroxyacyl radical (two-carbon surrogate for RCO_3)
APRC	Aromatic product carbon
ARO	Aromatic ring
ARPI	Aromatic oxidation intermediate product
CARB	Carbonyl bond
CBM	Carbon-Bond Mechanism
CRIG	Criegee intermediate (H_2CO_2)
CRO_2	Carbonyl peroxy which will produce DCRB
DCRB	Dicarbonyl compound
EKMA	Empirical Kinetics Modeling Approach
ETH	Ethylene or slow olefinic bond
GLY	Surrogate for dicarbonyls
KET	Ketone
MCRG	Surrogate for $RCHO_2$ type Criegee intermediates
MEO_2	Peroxy radical (one-carbon surrogate for RO_2)
NMHC	Non-methane hydrocarbon
NPHN	Nitrophenol
NRAT	Organic nitrate
OLE	Olefinic bond
OPEN	Aromatics ring-opening intermediate
OZIPM	Same as OZIPP plus mechanism and other options

OZIPP	Ozone Isopleth Plotting Package (computer program used in EKMA)
PAN	Peroxyacyl nitrate
PAR	Single or paraffinic bond
PHEN	Phenolic pathway surrogate in ARO oxidation
PHO	Phenoxy radical
...	General organic moiety (R = H, CH_3, C_2H_3, etc.)
RAO_2	Hydroxy peroxyl from OH + OLE
RARO	Aromatic radical
RBO_2	Hydroxyperoxyl from OH + ETH
RCO_3	Peroxyacyl radical
RHC	Reactive hydrocarbons
RO	Alkoxyl radical
RO_2	Peroxy radical
W	Carbonyl balancing unit
X	Carbon-mass balancing unit

SECTION 1

INTRODUCTION

The Carbon-Bond Mechanism (CBM) is a photochemical kinetic mechanism that has been developed expressly to provide a reasonable compromise between chemical realism and computational efficiency. The CBM is designed to meet stringent validation standards in the simulation of laboratory smog-chamber studies; however, it can also be easily applied to atmospheric studies using a minimum number of assumptions.

The version of the Carbon-Bond Mechanism presented in this manual is the product of two major revisions and is referred to as CBM-III. The original Carbon-Bond Mechanism (CBM-I) is described in Whitten, Hogo, and Killus (1980), and CBM-II is described in Whitten, Killus, and Hogo (1980). The current version (CBM-III) differs from CBM-II principally in the structure of the oxidation mechanism for aromatic hydrocarbons and in some modifications of inorganic reaction-rate constants.

These three Carbon-Bond Mechanisms are so named because they treat the carbon bond, rather than the molecule, as the principal unit of reaction. This concept offers several important advantages. First, the CBM is carbon-conservative. The olefinic bond group, for example, always contains two carbon atoms that must be accounted for in its products. The paraffinic bond contains one carbon atom, and the aromatic bonds, six.* Thus we can eliminate the cumbersome notion of "average molecular weight," which causes considerable difficulty in the application of lumped molecular mechanisms. Furthermore, use of the CBM allows precise calculation of carbon-mass balance in simulations, whereas such calculations can only be approximated when other mechanisms are used.

The second major advantage afforded by the CBM is a considerable reduction in the range of reaction-rate constants that must be averaged for the lumped hydrocarbon species. This is true for paraffins, for example, in which iso-butane has a molecular reaction-rate constant with OH of

---

* CBM-I treated aromatic bonds as a sum of three double-bonded carbon atoms. This approximation was changed in the CBM-II.

5000 $ppm^{-1}min^{-1}$, and iso-octane has a reaction rate of 11,500 $ppm^{-1}min^{-1}$. These reactivity rates, normalized to the number of carbon atoms per molecule, are 1250 $ppm^{-1}min^{-1}$ and 1440 $ppm^{-1}min^{-1}$, respectively. The relative difference between these two figures is thus much smaller than the relative difference between the molecular reaction rates.

Finally, because the CBM has been used for a wide variety of laboratory and atmospheric applications, the validation data set is extensive. Past performance has shown the CBM to be an eminently practical simulation tool. Each update of the mechanism is carefully considered in the light of past applications and current knowledge. The newer version of the CBM, therefore, should yield results similar to those obtained in past applications in which the older versions were used, but the recently modified CBM is more representative of current knowledge of the explicit photochemistry of smog formation.

SECTION 2

RECOMMENDATIONS

When using the CBM, special attention should be given to the level of carbonyls used in the inputs for emissions and air quality. Also, air monitoring data should be used to verify both the carbonyl inputs and the levels generated by the model using the CBM. Future validation studies for any atmospheric kinetics mechanism should involve comparisons of measured and simulated carbonyl levels.

Future versions of the CBM should include the correct chemistry for natural hydrocarbon species such as isoprene and α-pinene. This improvement will become possible as the explicit chemistry for these species becomes available.

SECTION 3

FORMULATION OF THE NEW VERSION OF THE CARBON-BOND MECHANISM

At the time the original CBM (shown in table 1) was formulated, it represented a condensation of existing explicit mechanisms (primarily for propylene and butane). It was also used to simulate a set of smog-chamber experiments with a reasonable degree of success. Knowledge of smog chemistry has expanded to include more molecules, however, and the amount of data derived from smog-chamber experiments has increased. Therefore, we sought to improve the Carbon-Bond Mechanism.

Periodic updating of generalized mechanisms like the CBM is preferable to continuous updating. Changes in one reaction may require compensating changes in other reactions to maintain the overall predictive accuracy of simulations in which the mechanism is used. Consequently, after a reaction change, the mechanism should be tested with an entire set of smog-chamber data to ensure that no special problems have arisen that would make atmospheric applications difficult. The cost of such testing makes it desirable to test the effects of several changes at once. Documentation of any changes is also necessary to keep all users of the mechanism informed.

For many applications (such as the use of the mechanism in a photochemical dispersion model) major changes in the mechanism require extensive program modification. Numerical changes in rate constants can be typically accommodated by such programs, but changes in product yield may involve modification of the steady-state approximations necessary for rapid solution of the chemical equations.

The first update of the CBM (CBM-II), reported by Whitten et al. (1979), reflected the following changes to the CBM formulation:

- Eliminating the peroxyformyl radical ($HCO_3^{\bullet}$).
- Updating the rate constants and excluding HONO and HOOH.
- Including the reactions of intermediate Criegee species formed from ozone-olefin reactions.

TABLE 1. THE ORIGINAL FORMULATION OF THE CARBON-BOND MECHANISM

	Reaction	Rate Constant ($ppm^{-1}min^{-1}$)
1	$NO_2 + h\upsilon \rightarrow NO + O$	*†
2	$O + O_2 (+ M) \rightarrow O_3 (+ M)$	2.08×10^{-5}
3	$O_3 + NO \rightarrow NO_2 + O_2$	25.2
4	$O + NO_2 \rightarrow NO + O_2$	1.34×10^{4}
5	$O_3 + NO_2 \rightarrow NO_3 + O_2$	5×10^{-2}
6	$NO_3 + NO \rightarrow NO_2 + NO_2$	1.3×10^{4}
7	$NO_3 + NO_2 + H_2O \rightarrow 2HNO_3$	1.66×10^{-3}§**
8	$NO + NO_2 + H_2O \rightarrow 2HNO_2$	2.2×10^{-9}§
9	$HNO_2 + h\upsilon \rightarrow NO + OH$	†
10	$NO_2 + OH\cdot \rightarrow HNO_3$	9×10^{3}
11	$NO + OH\cdot \rightarrow HNO_2$	9×10^{3}
12	$CO + OH\cdot \rightarrow CO_2 + HO_2\cdot$	2.06×10^{2}
13	$OLE + OH\cdot \xrightarrow{O_2} HCHO + CH_3O_2\cdot$	3.8×10^{4}
14	$PAR + OH\cdot \xrightarrow{O_2} CH_3O_2\cdot + H_2O$	1.3×10^{3}
15	$ARO + OH\cdot \xrightarrow{O_2} HCHO + CH_3O_2\cdot$	8×10^{3}
16	$OLE + O \xrightarrow{2O_2} HC(O)O_2\cdot + CH_3O_2\cdot$	5.3×10^{3}
17	$PAR + O \xrightarrow{O_2} CH_3O_2\cdot + OH\cdot$	20
18	$ARO + O\cdot \xrightarrow{2O_2} HC(O)O_2\cdot + CH_3O_2\cdot$	37
19	$OLE + O_3 \xrightarrow{O_2} HC(O)O_2\cdot + HCHO + OH\cdot$	0.01

(continued)

TABLE 1

	Reaction	Rate Constant ($ppm^{-1}min^{-1}$)
20	$ARO + O_3 \xrightarrow{O_2} HC(O)O_2^{\bullet} + HCHO + OH\bullet$	0.002
21	$OLE + O_3 \rightarrow$ Ozonide	0.005
22	$HCHO + h\upsilon \xrightarrow{2O_2} HC(O)O_2^{\bullet} + HO_2^{\bullet}$	†
23	$HCHO + h\upsilon \rightarrow CO + H_2$	4×10^{-4}*
24	$HCHO + OH\bullet \xrightarrow{O_2} HC(O)O_2^{\bullet} + H_2O$	1×10^{4}
25	$HO_2^{\bullet} + NO \rightarrow OH\bullet + NO_2$	2×10^{3}
26	$CH_3O_2^{\bullet} + NO \rightarrow NO_2 + HCHO + HO_2^{\bullet}$	2×10^{3}
27	$HC(O)O_2^{\bullet} + NO \rightarrow NO_2 + CO_2 + HO_2^{\bullet}$	2×10^{3}
28	$H_2O_2 + h\upsilon \rightarrow OH\bullet + OH\bullet$	†
29	$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2$	4×10^{3}
30	$CH_3O_2^{\bullet} + HO_2^{\bullet} \rightarrow H_3COOH + O_2$	4×10^{3}
31	$HC(O)O_2^{\bullet} + HO_2 \rightarrow HC(O)OOH + O_2$	1×10^{4}
32	$HC(O)O_2^{\bullet} + NO_2 \rightarrow PAN$	50
33	$PAN \rightarrow HC(O)O_2^{\bullet} + NO_2$	0.02*
34	$ARO + NO_3 \rightarrow$ Products	50
35	$HO_2^{\bullet} + NO_2 \rightarrow HNO_2$	20

* Units of min^{-1}.

† Light-dependent.

§ Units of $ppm^{-2}min^{-1}$.

** Rate constant is for the computer simulations of UCR smog-chamber experiments.

(concluded)

- Including new surrogate species representing the addition products of OH• to double bonds.

- Including a new formulation for carbonyl photolysis and oxidation.

- Treating alkyl radicals in long-chain paraffins.

- Treating ethylene as an explicit species.

- Treating internal olefins as carbonyls.

- Using a root-mean-square rate constant for the reactions of OH•, O, and O_3 with hydrocarbon mixtures.

- Incorporating a new aromatic chemical reaction scheme.

The rate constants used in the aromatics chemistry were modified by Whitten, Killus, and Hogo (1980). The aromatics scheme developed in CBM-II represented an interim treatment, occasioned by a rapid increase in our understanding of aromatic hydrocarbon oxidation. The second update of the CBM, discussed in this report, reformulates the aromatics chemistry to reflect current understanding of the explicit chemistry of toluene and xylenes. This revision also includes reactions that treat the oxidation of ketones to dicarbonyl compounds. Each of these changes is discussed in the following subsections.

The mechanism reported by Whitten, Killus, and Hogo (1980) (reflecting the first update plus rate-constant changes for aromatics) is known as CBM-II (see table 2); the new version of the Carbon-Bond Mechanism, shown in table 3, is called CBM-III.

ELIMINATION OF THE PEROXYFORMYL RADICAL

At the time of the original formulation of the CBM, our explicit mechanisms included the peroxyformyl radical ($HCO_3^\bullet$), which no longer appears in our explicit chemistry. To account for this change, we introduced a new species, $ACO_3^\bullet$, which is a surrogate for $RCO_3^\bullet$ radicals (where R has one or more carbon atoms). $ACO_3^\bullet$, which has two carbon atoms, is formed in the CBM from the reaction of OH• with the species CARB, which represents only one carbon atom. Thus some correction must be made to preserve carbon-mass balance. The correction we used is suggested by a reaction of $RCO_3^\bullet$ in the explicit mechanisms. In such mechanisms, $RCO_3^\bullet$ ($R > CH_3$) can react with NO to produce NO_2, CO_2, and $RO_2^\bullet$. The significance of that reaction is that it initiates the oxidation of the carbon atom adjacent to the $CO_3^\bullet$ group in $RCO_3^\bullet$ without any

TABLE 2. CARBON-BOND MECHANISM-II

	Reaction	Rate Constant at 298K* ($ppm^{-1}min^{-1}$)	Activation Energy (K)
1	$NO_2 + h\upsilon \rightarrow NO + O$	Experimental†	--
2	$O + O_2 + M \rightarrow O_3 + M$	2.1×10^{-5}§	--
3	$O_3 + NO \rightarrow NO_2 + O_2$	23.9	1,450
4	$O_3 + NO_2 \rightarrow NO_3 + O_2$	4.8×10^{-2}	2,450
5	$O + NO_2 \rightarrow NO + O_2$	1.34×10^{4}	--
6	$O_3 + OH \rightarrow HO_2 + O_2$	7.7×10^{1}	1,000
7	$O_3 + HO_2 \rightarrow OH + 2O_2$	5.0	1,525
8	$NO_2 + OH \rightarrow HNO_3$	1.4×10^{4}	--
9	$CO + OH \xrightarrow{O_2} HO_2 + CO_2$	4.4×10^{2}	--
10	$NO + NO + O_2 \rightarrow 2NO_2$	7.1×10^{-10}§	--
11	$NO_3 + NO \rightarrow 2NO_2$	2.8×10^{4}	--
12	$NO_3 + NO_2 + H_2O \rightarrow 2HNO_3$	$311 \times k(N_2O_5 + H_2O)$**	-10,600
13	$HO_2 + NO \rightarrow NO_2 + OH$	1.2×10^{4}	--
14	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	1.5×10^{4}	--
15	$PAR + O \xrightarrow{O_2} MEO_2 + OH$	2×10^{1}	2,100
16	$PAR + OH \xrightarrow{O_2} MEO_2 + H_2O$	1.5×10^{3}	560
17	$OLE + O \xrightarrow{O_2} MEO_2 + ACO_3 + X$	2.7×10^{3}	325
18	$OLE + O \rightarrow CARB + PAR$	2.7×10^{3}	325

(continued)

TABLE 2

	Reaction	Rate Constant at 298K* ($ppm^{-1}min^{-1}$)	Activation Energy (K)
19	$OLE + OH \xrightarrow{O_2} RAO_2$	4.2×10^4	-540
20	$OLE + O_3 \rightarrow CARB + CRIG$	8×10^{-3}	1,900
21	$OLE + O_3 \rightarrow CARB + MCRG + X$	8×10^{-3}	1,900
22	$ETH + O \xrightarrow{O_2} MEO_2 + HO_2 + CO$	6×10^2	800
23	$ETH + O \rightarrow CARB + PAR$	6×10^2	800
24	$ETH + OH \xrightarrow{O_2} RBO_2$	1.2×10^4	-382
25	$ETH + O_3 \rightarrow CARB + CRIG$	2.4×10^{-3}	2,560
26	$ACO_3 + NO \xrightarrow{O_2} NO_2 + MEO_2 + CO_2$	3.8×10^3	--
27	$RBO_2 + NO \xrightarrow{O_2} NO_2 + 2\ CARB + HO_2$	1.2×10^4	--
28	$RAO_2 + NO \xrightarrow{O_2} NO_2 + 2\ CARB + HO_2$	1.2×10^4	--
29	$MEO_2 + NO \xrightarrow{O_2} NO_2 + CARB + MEO_2 + X$	$(1.2 \times 10^4)(A-1)/A$ ††	--
30	$MEO_2 + NO \xrightarrow{O_2} NO_2 + CARB + HO_2$	$(1.2 \times 10^4)/A$ **	--
31	$MEO_2 + NO \rightarrow$ Nitrate	5×10^2	--
32	$RBO_2 + O_3 \rightarrow 2\ CARB + HO_2 + O_2$	5.0	--
33	$RAO_2 + O_3 \rightarrow 2\ CARB + HO_2 + O_2$	2×10^2	--
34	$MEO_2 + O_3 \rightarrow CARB + HO_2 + O_2$	5.0	--
35	$CARB + OH \xrightarrow{O_2} \alpha(HO_2 + CO) + (1 - \alpha)(ACO_3 + X)$	$(2.4 - \alpha) \times 10^4$	--
36	$CARB + h\upsilon \rightarrow CO + H_2$	αk_f *§§	--
37	$CARB + h\upsilon \xrightarrow{O_2} (1 + \alpha)HO_2 + (1 - \alpha)(MEO_2 + X) + CO$	$(\frac{\alpha + 1}{2})k_f$ *††	--
38	$X + PAR \rightarrow$	1×10^5	--

(continued)

TABLE 2

	Reaction	Rate Constant at 298K* ($ppm^{-1}min^{-1}$)	Activation Energy (K)
39	$ACO_3 + NO_2 \rightarrow PAN$	2×10^3	--
40	$PAN \rightarrow ACO_3 + NO_2$	2.8×10^{-2}†	12,500
41	$ACO_3 + HO_2 \rightarrow$ Stable products	4×10^3	--
42	$MEO_2 + HO_2 \rightarrow$ Stable products	4×10^3	--
43	$CRIG + NO \rightarrow NO_2 + CARB$	1.2×10^4	--
44	$CRIG + NO_2 \rightarrow NO_3 + CARB$	8×10^3	--
45	$CRIG + CARB \rightarrow$ Ozonide	2×10^3	--
46	$MCRG + NO \rightarrow NO_2 + CARB + PAR$	1.2×10^4	--
47	$MCRG + NO_2 \rightarrow NO_3 + CARB + PAR$	8×10^3	--
48	$MCRG + CARB \rightarrow$ Ozonide	2×10^3	--
49	$CRIG \rightarrow CO + H_2O$	6.7×10^{2}†	--
50	$CRIG \rightarrow$ Stable products	2.4×10^{2}†	--
51	$CRIG \xrightarrow{O_2} 2HO_2 + CO_2$	9×10^{1}†	--
52	$MCRG \rightarrow$ Stable products	1.5×10^{2}†	--
53	$MCRG \xrightarrow{O_2} MEO_2 + OH + CO$	3.4×10^{2}†	--
54	$MCRG \xrightarrow{O_2} MEO_2 + HO_2 + CO_2$	4.25×10^{2}†	--
55	$MCRG \xrightarrow{O_2} CARB + 2HO_2 + CO$	8.5×10^{1}†	--
56	$ARO + OH \xrightarrow{O_2} ARPI + ARPI + ARPI + HO_2$	6×10^3	--
57	$ARO + OH \xrightarrow{O_2} HO_2 + GLY + X$	1.6×10^3	--
58	$ARO + OH \xrightarrow{O_2} OH + GLY + W$	1.5×10^4	--
59	$W + CARB \rightarrow$	1.0×10^5	--
60	$ARPI + NO \rightarrow NO + CARB + PAR$	30	--

(continued)

TABLE 2

	Reaction	Rate Constant at 298K* ($ppm^{-1}min^{-1}$)	Activation Energy (K)
61	ARPI + NO → NO_2 + Aerosol	15	--
62	ARPI + NO_3 → CARB + CARB	3.5×10^4	--
63	ARPI + O_3 → Aerosol	0.6	--
64	GLY + OH → HO_2 + ARPI + ARPI + ARPI + CO	10^4	--
65	GLY $\xrightarrow{O_2}$ MEO_2 + HO_2 + ARPI + ARPI + ARPI	k_{GLY}***	--

* The rate constants shown were those employed at UCR to model eleven experiments in which mixes of seven hydrocarbons were used. For that study the default values $\alpha = 0.5$ and $A = 1.3$ were used.

† Units of min^{-1}.

§ Units of $ppm^{-2}min^{-1}$.

** $k(N_2O_5 + H_2O) = 5 \times 10^{-6}$ $ppm^{-1}min^{-1}$ for UCR simulations.

†† A = A is the average number of $RO_2^{\bullet}$-type radicals generated from a hydrocarbon between attack by OH• and generation of $HO_2^{\bullet}$.

§§ α is the fraction of total aldehydes that represents formaldehyde and ketones. k_f is the carbonyl photolysis rate constant.

*** $k_{GLY} \cong 0.036 \times k_{(NO_2 + h\upsilon)}$.

(concluded)

TABLE 3. CARBON-BOND MECHANISM III

	Reaction	Rate Constant at 298K ($ppm^{-1}min^{-1}$)	Activation Energy (K)
1	$NO_2 \rightarrow NO + O$	*	0
2	$O + (O_2) + (M) \rightarrow O_3$	4.40×10^{6}†	0
3	$NO + O_3 \rightarrow NO_2 + O_2$	26.6	1450
4	$NO_2 + O_3 \rightarrow NO_3 + O_2$	0.048	2450
5	$NO_2 + O \rightarrow NO + O_2$	1.3×10^{4}	0
6	$OH + O_3 \rightarrow HO_2 + O_2$	100	1000
7	$HO_2 + O_3 \rightarrow OH + 2O_2$	2.40	1525
8	$OH + NO_2 \rightarrow HNO_3$	1.60×10^{4}	0
9	$OH + CO \xrightarrow{O_2} HO_2 + CO_2$	440	0
10	$NO + NO + (O_2) \rightarrow NO_2 + NO_2$	1.50×10^{-4}†	0
11	$NO + NO_3 \rightarrow NO_2 + NO_2$	2.80×10^{4}	0
12	$NO_2 + NO_3 + H_2O \rightarrow 2HNO_3$	§	-1.06×10^{4}
13	$NO + HO_2 \rightarrow NO_2 + OH$	1.20×10^{4}	0
14	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	1.50×10^{4}	0
15	$X + PAR \rightarrow$	10^{5}	0
16	$OH + PAR \xrightarrow{O_2} MEO_2 + H_2O$	1300	560
17	$O + OLE \xrightarrow{O_2} MEO_2 + ACO_3 + X$	2700	325
18	$O + OLE \rightarrow CARB + PAR$	2700	325
19	$OH + OLE \xrightarrow{O_2} RAO_2$	3.70×10^{4}	-540

(continued)

TABLE 3

	Reaction	Rate Constant at 298K ($ppm^{-1}min^{-1}$)	Activation Energy (K)
20	O_3 + OLE → CARB + CRIG	0.008	1900
21	O_3 + OLE → CARB + MCRG + X	0.008	1900
22	O + ETH $\xrightarrow{O_2}$ MEO_2 + HO_2 + CO	600	800
23	O + ETH → CARB + PAR	600	800
24	OH + ETH $\xrightarrow{O_2}$ RBO_2	1.20×10^4	-382
25	O_3 + ETH → CARB + CRIG	0.0024	2560
26	NO + ACO_3 $\xrightarrow{O_2}$ NO_2 + MEO_2	1.04×10^4	0
27	NO + RBO_2 $\xrightarrow{O_2}$ NO_2 + CARB + HO_2 + CARB	1.20×10^4	0
28	NO + RAO_2 $\xrightarrow{O_2}$ NO_2 + CARB + HO_2 + CARB	1.20×10^4	0
29	NO + MEO_2 $\xrightarrow{O_2}$ NO_2 + CARB + MEO_2 + X	3800	0
30	NO + MEO_2 $\xrightarrow{O_2}$ NO_2 + CARB + HO_2	7700	0
31	NO + MEO_2 → NRAT	500	0
32	O_3 + RBO_2 → CARB + CARB + HO_2 + O_2	5.0	0
33	O_3 + RAO_2 → CARB + CARB + HO_2 + O_2	200	0
34	OH + CARB → CRO_2 + X	500	0
35	OH + CARB $\xrightarrow{O_2}$ HO_2 + CO	7000	0
36	OH + CARB $\xrightarrow{O_2}$ ACO_3 + X	6000	0
37	CARB → CO + H_2	($\approx$0.001 K_1)*	0
38	CARB + (O_2) $\xrightarrow{O_2}$ 2/3 ($2HO_2$ + CO) 1/3 ($2MEO_2$ + CO + 2X)	($\approx$0.002 K_1)*	0

(continued)

TABLE 3

	Reaction	Rate Constant at 298K ($ppm^{-1}min^{-1}$)	Activation Energy (K)
39	$NO_2 + ACO_3 \rightarrow PAN$	7000	0
40	$PAN \rightarrow ACO_3 + NO_2$	0.022	1.35×10^4
41	$HO_2 + ACO_3 \rightarrow$ Stable products	1.50×10^4	0
42	$HO_2 + MEO_2 \rightarrow$ Stable products	9000	0
43	$NO + CRIG \rightarrow NO_2 + CARB$	1.20×10^4	0
44	$NO_2 + CRIG \rightarrow NO_3 + CARB$	8000	0
45	$CARB + CRIG \rightarrow$ Ozonide	2000	0
46	$NO + MCRG \rightarrow NO_2 + CARB + PAR$	1.20×10^4	0
47	$NO_2 + MCRG \rightarrow NO_3 + CARB + PAR$	8000	0
48	$CARB + MCRG \rightarrow$ Ozonide	2000	0
49	$CRIG \rightarrow CO + H_2O$	670**	0
50	$CRIG \rightarrow$ Stable products	240**	0
51	$CRIG \xrightarrow{O_2} HO_2 + HO_2 + CO$	90**	0
52	$MCRG \rightarrow$ Stable products	150**	0
53	$MCRG \xrightarrow{O_2} MEO_2 + OH + CO$	340**	0
54	$MCRG \xrightarrow{O_2} MEO_2 + HO_2$	425**	0
55	$MCRG \xrightarrow{O_2} CARB + HO_2 + CO + HO_2$	85**	0
56	$OH + ARO \xrightarrow{O_2} RARO + H_2O$	8000	600
57	$OH + ARO \xrightarrow{O_2} HO_2 + OPEN$	1.45×10^4	400
58	$NO + RARO \xrightarrow{O_2} NO_2 + PHEN + HO_2$	4000	0

(continued)

TABLE 3

	Reaction	Rate Constant at 298K ($ppm^{-1}min^{-1}$)	Activation Energy (K)
59	$OPEN + NO \xrightarrow{O_2} NO_2 + DCRB + X + APRC$	6000	0
60	$APRC \xrightarrow{O_2} DCRB + CARB + CO$	10^{4**}	0
61	$APRC \xrightarrow{O_2} CARB + CARB + CO + CO$	10^{4**}	0
62	$PHEN + NO_3 \rightarrow PHO + HNO_3$	5000	0
63	$PHO + NO_2 \rightarrow NPHN$	4000	0
64	$PHO + HO_2 \rightarrow PHEN$	5.00×10^4	0
65	$OPEN + O_3 \rightarrow DCRB + X + APRC$	40	0
66	$OH + PHEN \xrightarrow{O_2} HO_2 + APRC + PAR + CARB$	3.00×10^4	0
67	$DCRB \xrightarrow{O_2} 1/2\ (HO_2 + ACO_3 + CO)$ $1/2\ (MEO_2 + HO_2 + 2CO)$	$(\approx 0.04\ K_1)^*$	0
68	$PHEN + OH \rightarrow PHO$	10^4	0
69	$CRO_2 + NO \xrightarrow{O_2} NO_2 + HO_2 + DCRB$	1.20×10^4	0
70	$DCRB + OH \rightarrow ACO_3$	7000	0
71	$HONO \rightarrow OH + NO$	$(\approx 0.06\ K_1)^*$	0
72	$OH + NO \rightarrow HONO$	9770	0
73	$O_3 \rightarrow O^1D$	$(\approx 10^{-3} K_1)^*$	0
74	$O^1D \xrightarrow{+(M)} O$	4.44×10^{10}	0
75	$O^1D + H_2O \rightarrow OH + OH$	3.4×10^5	0

* Sunlight-dependent; units of min^{-1}.

† Units of $ppm^{-2}min^{-1}$.

§ Heterogeneous; pseudo third order. Equal to $591 \times N_2O_5 + H_2O$.

** Units of min^{-1}.

involvement of OH• or O. Thus it corresponds, in the terms used in the CBM, to the conversion of PAR (single or paraffinic bond) to MEO_2 (the surrogate for $RO_2^{\bullet}$)by a pathway not previously accounted for in the CBM. In the revised Carbon-Bond Mechanism, $ACO_3^{\bullet}$ reacts with NO to produce NO_2, CO_2, and MEO_2. When this reaction is included in the CBM, one PAR must be subtracted to account for the MEO_2 formed (i.e., to maintain carbon-mass balance). We accomplished this by means of a fictitious compound X. Whenever an extra carbon atom appears on the right side of a chemical reaction, one X is produced that immediately removes one PAR by means of the reaction PAR + X→ , which is given a high rate constant. Typically, the appearance of X accounts for the oxidation of a single-bonded carbon atom from the PAR pool by pathways other than direct reaction with OH• (oxidation of paraffins by oxygen atoms has been eliminated in the CBM-III). These other pathways were not accounted for in the original formulation of the CBM.

In using the methodology just described, one may encounter difficulty if X is produced when no saturated carbon atoms remain (i.e., [PAR] = 0). An example of such a case would be one in which the formaldehyde concentration is large compared with that of the paraffins and higher aldehydes. If it is known a priori that such a case exists, the formation rate of $ACO_3^{\bullet}$ can simply be set to a small number. However, it is unlikely that this situation will occur in the atmosphere, where paraffinic hydrocarbons are abundant. Tropospheric methane provides an equivalent minimum [PAR] level of 0.01 ppm.

In the application of complex atmospheric models, we have encountered situations in which a flaw in the numerical transport algorithm artificially reduced [PAR] to a low level (which was reduced to a negative number when the "X chemistry" was employed). However, we do not consider this to be a drawback in the treatment of chemistry. Indeed, in this instance the chemistry subroutine helped to locate an error in the transport algorithm.

PRODUCTS OF THE OZONE-OLEFIN REACTIONS

Because Criegee intermediates from the ozone-olefin reaction were added to the explicit mechanisms, we included them in the Carbon-Bond Mechanism. The Criegee intermediates are represented by the symbols CRIG for CH_2O_2 and MCRG for $CH_3CH_2O_2$, the two Criegee intermediates found in the explicit mechanisms (see Whitten et al., 1979, and Dodge and Arnts, 1979).

EXPLICIT TREATMENT OF THE OLEFIN HYDROXYL ADDITION PRODUCT

The explicit chemistry of hydroxyl attack on olefins leads to the formation of two aldehydes from the initial addition product, which in air is a $HORO_2$ radical. In CBM-I this radical was treated as a typical RO_2 radical

that produces but one aldehyde; the extra aldehyde was added along with the RO_2 as a product in the initial OH reaction. However, CBM-II and CBM-III include a special reaction of the $HORO_2$ addition product with O_3. Hence, the explicit treatment allows the formation of two aldehydes from the $HORO_2$ or reaction with O_3. The O_3 reaction is still under investigation, and future versions of the CBM probably will not require this reaction.

INORGANIC RADICAL SOURCES

Although the chemistries of HONO and O^1D (reactions 70 to 74) are included in CBM-III, these reactions can be deleted from the mechanism for most urban applications. The production and destruction of HONO is a relatively unimportant cycle, and the steady-state concentration of HONO during the day is very low. Small concentrations of HONO (1 to 2 ppb) have been measured at night (Platt et al., 1980), and the compound might be found in small concentrations in emitted NO_x. Although HONO is important in the initiation phase of smog-chamber experiments, other radical sources (e.g., HCHO) have been measured at concentrations high enough to overshadow the importance of HONO as a component of polluted air.

Ozone photolyzes to form O^1D, a fraction of which then reacts with water to generate OH (reactions 72 to 74). We have found this reaction to be important principally in application to rural areas, where the background concentration of ozone is greater than 10 times the background of carbonyl compounds. In urban applications O^1D chemistry is relatively unimportant and can often be omitted.

CARBONYL PHOTOLYSIS AND OXIDATION

A necessary part of the formulation of the Carbon-Bond Mechanism is the condensation of the reactions of aldehydes and ketones into two types of reactions, namely, photolysis and oxidation by hydroxyl radical.

In general, aldehydes larger than formaldehyde appear to photolyze as follows:

$$RCHO + h\upsilon \rightarrow R'O_2^{\cdot} + HO_2^{\cdot} + CO \qquad k_{(1)} = \phi k_f \quad . \qquad (1)$$

The photolysis rate constant ϕk_f is defined as follows: ϕ is the average quantum yield, and k_f is the photolysis rate constant for formaldehyde producing two radicals.

In the photolysis of formaldehyde under a typical solar spectrum, two reaction pathways occur at approximately equal rates:

$$HCHO + h\upsilon \rightarrow H_2 + CO \qquad k_{(2)} = k_f \quad , \qquad (2)$$

$$HCHO + h\upsilon \rightarrow HO_2\bullet + HO_2\bullet + CO \qquad k_{(3)} = k_f \quad . \qquad (3)$$

Thus the total photolysis rate for formaldehyde is 2 x k_f.

For simplicity, CBM-II treated ketone photolysis in the same manner as it would formaldehyde. The lumped reaction set for carbonyl photolysis then became

$$CARB + h\upsilon \rightarrow H_2 + CO \qquad k_{(4)} = \alpha k_f \quad , \qquad (4)$$

$$CARB + h\upsilon \rightarrow (1 + \alpha)HO_2\bullet \qquad (5)$$

$$+ (1 - \alpha)(MEO_2 + X) + CO \qquad k_{(5)} = \left(\frac{\alpha + 1}{2}\right) k_f \quad ,$$

where

$$\alpha = \frac{[\text{formaldehyde}] + [\text{ketones}]}{[\text{total carbonyls}]} \quad ,$$

and

k_f = formaldehyde photolysis to radicals,

= formaldehyde photolysis to stable products

1/2 k_f = photolysis of higher aldehydes.

More realistically, ketone photolysis typically yields two peroxyalkyl radicals:

$$KET + h\upsilon \rightarrow RO_2\bullet + RO_2\bullet + CO \quad . \qquad (5a)$$

Ketones can also yield peroxyacyl as a photolysis product:

$$KET + h\upsilon \rightarrow RO_2^{\bullet} + RCO_3^{\bullet} \quad . \tag{5b}$$

However, this is a minor formation pathway for peroxyacyl (hydroxyl attack on higher aldehydes has much greater significance). Since $RCO_3^{\bullet}$ yields $RO_2^{\bullet}$ when reduced by NO, equation (5a) is a good approximation of the overall process.

For the new lumped mechanism (CBM-III), we define CARB as the concentration of carbonyls (i.e., the sum of the aldehyde and ketone concentrations):

$$CARB + h\upsilon \rightarrow (H_2 + CO) = CO + H_2 \quad , \tag{6a}$$

$$CARB + h\upsilon \rightarrow (HO_2^{\bullet} + HO_2^{\bullet} + CO) = 2HO_2^{\bullet} + CO \quad , \tag{6b}$$

$$CARB + h\upsilon \rightarrow (MEO_2 + 2X + MEO_2^{\bullet} + CO) \quad , \tag{6c}$$

with the photolysis rate constants,

$$\frac{form}{CARB} \cdot k_{(1)} = k_{(6a)} \quad ,$$

$$\frac{[k_{(3)}]\ form + (0.5\ higher\ aldehydes)k_{(1)}}{CARB} = k_{(6b)} \quad ,$$

$$\frac{[k_{(1)}]\ (0.5\ higher\ aldehydes) + KET[k_{(5a)}]}{CARB} = k_{(6c)} \quad .$$

Thus, the higher aldehyde photolysis pathway is halfway between formaldehyde and ketones in product yield.

The second major reaction of aldehydes is oxidation by hydroxyl radicals:

$$HO_2^{\bullet} + CO + H_2O \quad \text{for formaldehyde} \tag{7a}$$

$$RCHO + OH^{\bullet} \rightarrow$$

$$ACO_3^{\bullet} + H_2O \quad \text{for higher aldehydes} \tag{7b}$$

Ketone oxidation is more complex. For example, (MEK)

$$CH_3COCH_2CH_3 + OH \xrightarrow{+O_2} CH_3COCHO_2^{\bullet}CH_3 + (H_2O) \quad , \tag{8}$$

$$CH_3COCHO_2^{\bullet}CH_3 + NO \rightarrow NO_2 + CH_3COCH\dot{O}CH_3 \quad , \tag{9}$$

$$CH_3COCH\dot{O}CH_3 + O_2 \rightarrow HO_2 + CH_3\ COCOCH_3 \quad \text{(biacetyl, a highly photolytic dicarbonyl compound).} \tag{10}$$

A ketone oxidation pathway can easily be included in CBM-III because the dicarbonyl compounds (DCRB) are already included as part of the new aromatics chemistry.

$$CARB + OH \rightarrow CRO_2 + X \quad , \tag{11}$$

$$CRO_2 + NO \rightarrow NO_2 + HO_2 + DCRB \quad . \tag{12}$$

Aldehyde oxidation pathways are the same for both CBM-II and CBM-III:

$$CARB + OH \rightarrow HO_2 + CO + H_2O \quad , \tag{13}$$

$$CARB + OH \rightarrow ACO_3 + X + H_2O \quad , \tag{14}$$

where X is the previously mentioned negative carbon species used to maintain mass balance.

ALKYL RADICAL CHEMISTRY

The alkyl radical (RO•) chemistry used in our mechanisms was discussed in detail by Whitten and Hogo (1977). In the propylene and butane explicit mechanisms, only alkyl radicals with four or fewer carbon atoms are important. The following reactions for the primary alkyl radicals are used in these explicit mechanisms:

$$CH_3CH_2CH(O\cdot)CH_3 \xrightarrow{O_2} CH_3CH_2O_2\cdot + CH_3CHO \qquad k = 1.0 \times 10^5\ min^{-1} \quad , \quad (15)$$

$$CH_3CH_2CH(O\cdot)CH_3 + O_2 \rightarrow CH_3CH_2C(O)CH_3 + HO_2\cdot \qquad k = 1.43\ ppm^{-1}min^{-1} \quad , \quad (16)$$

$$CH_3CH_2CH_2CH_2O\cdot \xrightarrow{O_2} HOCH_2CH_2CH_2CH_2O_2\cdot \qquad k = 2 \times 10^6\ min^{-1} \quad , \quad (17)$$

$$CH_3CH_2CH_2CH_2O\cdot + O_2 \rightarrow CH_3CH_2CH_2CHO + HO_2\cdot \qquad k = 3.3\ ppm^{-1}min^{-1} \quad , \quad (18)$$

$$CH_3CH_2CH_2O\cdot + O_2 \rightarrow CH_3CH_2CHO + HO_2\cdot \qquad k = 3.3\ ppm^{-1}min^{-1} \quad , \quad (19)$$

$$CH_3CH_2O\cdot + O_2 \rightarrow CH_3CHO + HO_2\cdot \qquad k = 3.3\ ppm^{-1}min^{-1} \quad , \quad (20)$$

$$CH_3O\cdot + O_2 \rightarrow HCHO + HO_2\cdot \qquad k = 1.2\ ppm^{-1}min^{-1} \quad . \quad (21)$$

Alkylperoxyl radicals can thus react through a number of pathways that may be represented as follows:

$$RO_2\cdot + NO \rightarrow RO\cdot + NO_2 \quad , \quad (22)$$

$$RO_2\cdot + NO \rightarrow \text{nitrates} \quad , \quad (23)$$

$$RO\cdot + O_2 \rightarrow \text{aldehyde} + HO_2\cdot \quad , \quad (24)$$

$$RO\cdot \xrightarrow{O_2} HORO_2\cdot \text{ (isomerization)} \quad , \quad (25)$$

$$RO\cdot \xrightarrow{O_2} R'O_2\cdot + \text{aldehyde (decomposition)} \quad , \quad (26)$$

$$RO_2\cdot + HO_2\cdot \rightarrow \text{stable products} \quad . \quad (27)$$

Reactions (25) and (26) occur in systems with carbon chains greater than, or equal to, four (e.g., butane and 2,3-dimethylbutane). The isomerization reaction chain (reaction 25) terminates when the α-hydroxyl radical reacts with oxygen to form a carbonyl compound--i.e., reaction (24). In the Carbon Bond Mechanism, we write reactions (22) and (24) as a single step:

$$MEO_2 + NO \rightarrow NO_2 + CARB + HO_2^{\cdot} \quad . \tag{28}$$

We have condensed reactions (25) and (26) into the $RO_2^{\cdot}$ scheme as:

$$MEO_2 + NO \rightarrow NO_2 + CARB + (MEO_2 + X) \quad . \tag{29}$$

Reactions (23) and (27) translate directly into:

$$MEO_2 + NO \rightarrow \text{nitrates} \quad , \tag{30}$$

$$MEO_2 + HO_2^{\cdot} \rightarrow \text{stable products} \quad . \tag{31}$$

Reaction (29) condenses the alkyl isomerization and decomposition processes, with the net effect that more than one $RO_2^{\cdot}$ radical is generated per reaction of PAR with OH. The condensed reaction sequence lumps the hydroxy-carbon group into the carbonyl category, an approximation whose validity cannot be assessed without explicit data for the reactivity of hydroxy compounds. However, isomerized hydroxy species have not yet been detected. Since a slow reaction rate would allow the buildup of detectable concentrations of these species, a relatively high reaction rate for such compounds is implied.

If we let "A" equal the number of $RO_2^{\cdot}$ radicals per alkyl oxidation, then

$$k_{(29)} = k_{(28)}(A - 1) \quad .$$

For short-chain hydrocarbons (carbon number <4) A = 1 and $k_{(29)} = 0$. The sum of the rate constants for reactions (28), (29), and (30) equals the reaction rate of $RO_2^{\cdot} + NO$:

$$k_{(28)} + k_{(29)} + k_{(30)} = 12{,}000 \text{ ppm}^{-1}\text{min}^{-1} \quad .$$

Therefore,

$$k_{(29)} = [12{,}000 - k_{(30)}] \frac{A - 1}{A} \quad .$$

Empirically, nitrate formation observed in smog-chamber experiments requires a reaction-rate constant for reaction (30) that falls within the range of 250 $ppm^{-1}min^{-1}$ to 1250 $ppm^{-1}min^{-1}$, depending on the hydrocarbons involved. For an intermediate urban mix of hydrocarbons, we recommend a rate of 500 $ppm^{-1}min^{-1}$. Long chain alkyl radicals tend to react according to the pathways shown in reactions (29) and (30) more often than do molecules having lower molecular weight. Insufficient information is available to set these reaction-rate constants a priori; Carter et al. (1979) suggested some values for individual peroxy radicals on the basis of empirical fits to smog-chamber data.

For some hydrocarbons (e.g., 2,3-dimethylbutane) "A" can be as high as 2. When calculations for butane are based on the detailed reaction sequence, "A" is approximately 1.3. Calculations based on the ratio of hydrocarbon consumed to the oxidation of NO in smog-chamber experiments (Kopczynski, Kuntz, and Bufalini, 1975) yield a value for "A" of 1.5, which we recommend as the default value for "A". Therefore, the nominal rate constants for reactions (28), (29), and (30) are 7700, 3800, and 500, respectively.

AROMATIC OXIDATION

We have devised an explicit mechanism for treating toluene oxidation (Killus and Whitten, 1981) and have extended our work to include simulation of m-xylene systems. Our studies indicate that aromatic hydrocarbon oxidation differs from olefin and paraffin oxidation in several important ways. Our simulation mechanisms show three major differences between aromatic compounds and a compound such as propylene:

> A high photolysis rate of oxidation products: toluene oxidation products, for example, photolyze at a rate twice that which would result from a 100 percent yield of formaldehyde from toluene decay. This high rate is apparently caused by a fractional yield of methyl glyoxal,

which photolyzes at a rate roughly 15 times that of formaldehyde.

> A low rate of peroxyl radical production: the inefficiency of toluene and other aromatic hydrocarbons in effecting NO-to-NO_2 conversions has been observed by other investigators (Kopczynski, Kuntz, and Bufalini, 1975). Empirically, methyl glyoxal photolysis alone is nearly sufficient to explain the number of NO-to-NO_2 conversions observed in toluene oxidation. Thus, either the other products of toluene decay are unreactive or there is a mechanism in toluene oxidation that destroys peroxyl or otherwise prevents the peroxyl radicals from reacting with NO.

> After the onset of ozone production, a powerful NO_x sink mechanism occurs that does not appear to consume hydrogen-containing radicals. This sink probably involves NO_3^* and can result in nitrophenols or dinitrate compounds.

The mechanism described herein contains the aforementioned features and is based on a condensation of our explicit aromatics mechanisms.

RING OPENING

The initial step of the ring opening pathway can be easily treated with three reactions:

$$ARO + OH \rightarrow OPEN \quad , \tag{32}$$

$$OPEN + NO \rightarrow NO_2 + HO_2 + DCRB + APRC \quad , \tag{33}$$

$$OPEN + O_3 \rightarrow HO_2 + DCRB + APRC \quad . \tag{34}$$

These reactions are exactly analogous to reactions in our explicit toluene mechanism. The lumped rate constant of initial OH attack depends on the mix of hydrocarbons present.

The species DCRB represents photolyzable dicarbonyl species: methyl glyoxal and biacetyl.

The species APRC (aromatic product carbon) represents the remainder of the aromatic molecule once the dicarbonyl species has been subtracted. In toluene oxidation this would be either the compound cis-2-butenedial (CBD) or two glyoxal molecules, depending on the degree of oxidation of the aromatic molecule prior to ring opening. Since xylene has another methyl group attached to the ring, the ultimate yield of methyl glyoxal is twice that of toluene but depends on the xylene isomer.

We treat the secondary products represented by APRC in a simple way:

$$\text{APRC} \rightarrow \text{DCRB} + \text{GLY} \quad , \tag{35}$$

$$\text{APRC} \rightarrow \text{GLY} + \text{GLY} \quad . \tag{36}$$

Thus far we have obtained the best results using a 50/50 split to pathways (35) and (36) for experiments containing equal amounts of toluene and xylene.

We have the following oxidation sequence for glyoxal:

$$(\text{CHO})_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{HCO} + \text{CO} \quad , \tag{37}$$

$$\text{HCO}\cdot \rightarrow \text{HO}_2 + \text{CO} \quad . \tag{38}$$

This sequence is similar to that of formaldehyde oxidation except for the extra yield of 1 molecule of CO. Therefore, we treat the production of glyoxal in the carbon-bond units as

$$\text{GLY} = \text{CARB} + \text{CO} \quad .$$

PATHWAYS TO PHENOLIC HYDROCARBONS

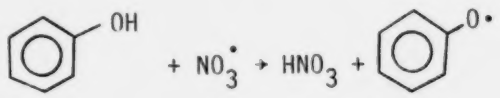
In our toluene mechanism there are two pathways to phenolic hydrocarbons: (1) addition of OH to the aromatic ring, forming cresols, and (2) hydration and nitrification of oxybenzoyl radicals. One example of the second pathway is the terminating reactions of benzaldehyde (BZA) oxidation:

$$\text{BZA} + \text{OH} \xrightarrow{+\text{O}_2} \text{peroxyl benzoyl } (\text{PBZO}_2) \quad , \tag{39}$$

$$\text{PBZO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{oxybenzoyl (PBZO)} \quad , \tag{40}$$

$$PBZO + NO_2 \xrightarrow{+\ water} \text{nitrophenol (NPHN)} \quad . \qquad (41)$$

Phenolic hydrocarbons may serve as both radical sinks and NO_x sinks in our reaction scheme. NO_x is lost from the system in the form of nitrophenols and also when $NO_3^{\bullet}$ is converted to nitric acid:



. (42)

Hydrogen abstraction from the paraffinic substituents on the aromatic ring is treated in the single-bonded carbon portion of the Carbon-Bond Mechanism. Similarly, the carbonyl portion of benzaldehyde is lumped together with the carbonyl bonds, and peroxybenzoyl nitrate is lumped with other PANS. The phenolic pathway of BZA oxidation is lumped with OH addition to the aromatic ring:

$$ARO + OH \rightarrow RARO \text{ (aromatic radical)} \quad , \qquad (43)$$

$$RARO + NO \rightarrow NO_2 + HO_2 + PHEN \quad . \qquad (44)$$

The lumped species PHEN can then react with OH or NO_3 to form nitrophenols:

$$PHEN + OH \rightarrow PHO_3 \quad , \qquad (45)$$

$$PHEN + NO_3 \rightarrow PHO + HNO_3 \quad , \qquad (46)$$

$$PHO + NO_2 \rightarrow NPHN \quad . \qquad (47)$$

Since nitrophenols have low vapor pressures, it is likely that they also participate in aerosol formation.

The phenoxy radical can also react with HO_2:

$$PHO + HO_2 \rightarrow PHEN + O_2 \quad . \qquad (48)$$

This reaction can be an important radical sink in aromatic systems. We assume that the reaction rate for this reaction is similar to that of OH + HO_2 (Baulch et al., 1980).

SECTION 4

USING THE CARBON-BOND MECHANISM

In its current form, the Carbon-Bond Mechanism (CBM-III) treats the reactions of six types of carbon atoms: (1) single-bonded carbon atoms, whose principal constituent is paraffinic carbon molecules (hence the abbreviation PAR), (2) relatively reactive double-bonded carbon (OLE), (3) slow double bonds, which are almost exclusively ethylene (ETH), (4) reactive aromatic rings (ARO), (5) carbonyl compounds such as aldehydes and ketones (CARB), and (6) highly photolytic α-dicarbonyl compounds such as methyl glyoxal and biacetyl (DCRB). Some other types of carbon atoms can also be treated within this set. For instance, highly reactive internal double-bonded carbon atoms were shown by Whitten, Killus, and Hogo (1980) to be equivalent to two carbonyls per double bond. Hence three levels of olefin reactivity can be treated in the CBM (slow as ETH, relatively reactive terminal olefins as OLE, and highly reactive internal olefins as 2 CARB per bond). Appendix B lists the CBM fractions recommended for a variety of organics.

The use of the molecular bond rather than the whole molecule as the principal unit may at first seem confusing to those whose experience is solely with molecular reactions. However, several major advantages associated with the bond-group-reaction principle make the conceptual effort involved worthwhile.

The primary advantage is that the Carbon-Bond Mechanism does not require the sometimes uncertain calculation of "average molecular weight." The carbon number of each carbon-bond group is fixed:

Carbon-Bond Group	Carbon Number (carbon atoms)
PAR	1
ETH	2
OLE	2
ARO	6
CARB	1 (plus 1 oxygen atom)
DCRB	2 (plus 2 oxygen atoms)

In a lumped molecular mechanism, chemical reactions might be expected to alter the average molecular weight of each species category. When this phenomenon occurs, it is impossible to perform mass-balance calculations on the reactive organic compounds remaining in the model simulation. The Carbon-Bond Mechanism allows precise hydrocarbon-mass-balance calculations to be made, thus facilitating the estimation of the importance of phenomena like long-range smog precursor transport and day-to-day carry-over of pollutants. Moreover, whereas most lumped molecular mechanisms do not conserve carbon, the Carbon-Bond Mechanism conserves carbon and follows each hydrocarbon fraction to its end products (generally CO or CO_2, but occasionally aerosol or nonreactive hydrocarbons).

The range of reactivities of carbon bonds is generally less than that of reactivities of molecules because larger molecules tend to react faster even if each constituent atom is of similar reactivity. Thus the problem of rate-constant averaging is reduced in the Carbon-Bond Mechanism.

The carbon-bond concept has an additional advantage over the molecular concept because it offers a sensible method for dealing with the atmospheric chemistry of many complex or unusual molecules. For example, the molecule cinnamaldehyde ($C_6H_5CH{=}CHCHO$) might be treated as 1 ARO, 1 OLE, and 1 CARB assuming that the double bond is about as reactive as propylene. The double bond can also be treated as 1 ETH or 2 CARB, depending on the extent of its reactivity compared with that of propylene. For mechanisms in which the molecular concept is used, cinnamaldehyde can be described as an aromatic, an olefin, or an aldehyde. In making a choice among the three possibilities, the chemistry associated with the other two parts of the molecule is ignored, whereas the CBM approach offers reasonable chemical pathways for all three parts. Some surrogate mechanisms use a particular blend of propylene and butane to provide a reasonable simulation fit to smog-chamber data in which cinnamaldehyde is used. However, in the absence of smog-chamber data the surrogate and molecular approaches require arbitrary decisions, whereas the

carbon-bond approach provides a simple methodology for handling a large variety of molecules. The current carbon-bond approach allows some flexibility to adjust reactivity should smog-chamber data or other information become available (as in the cinnamaldehyde example).

Another related advantage of the carbon-bond approach over the molecular or surrogate approaches is optimization for simulating complex mixes rather than single molecules. The current CBM is designed to be optimized for simulating urban mixtures of hydrocarbons. If used for single-molecule smog-chamber experiments, the CBM requires certain adjustments that are usually straightforward. Molecular or surrogate mechanisms, on the other hand, are inherently optimized to simulate smog-chamber experiments using only the specific molecules that form the basis of the mechanisms. Thus, simulating complex urban mixes with these mechanisms requires adjustments in both the precursor definitions and the chemistry, and such adjustments are often complicated.

Finally, the Carbon-Bond Mechanism in its present implementation (CBM-III) has several features that enable us to recommend it over other available mechanisms. For example, treating ethylene as a separate species is an improvement over lumping all olefins together, because the behavior of olefins varies greatly with changing olefinic composition. The treatment of aromatic hydrocarbons in CBM-III is more chemically realistic than that in previous mechanisms. However, a realistic treatment of ethylene and aromatic hydrocarbons is not inherent in the carbon-bond concept. Molecular mechanisms can also be designed with similar features; at the present time only the CBM-III has been so designed.

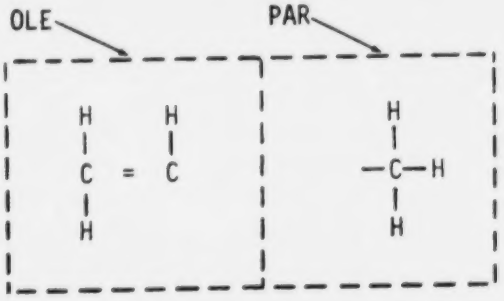
SPECIATION OF EMISSIONS AND ATMOSPHERIC CONCENTRATIONS INTO BOND CATEGORIES

Several important principles must be remembered in the application of the Carbon-Bond Mechanism. First, all carbon must be accounted for. Thus, if one adds up all of the carbon in each bond category of emissions, the sum should equal the total carbon emitted. Although this principle appears simple and obvious, there are practical complications. Emissions of solvents, for example, are usually given in kilograms of emissions, but methyl alcohol (H_2COH) is a solvent in which most of the weight is represented by the oxygen atom in the methanol molecule. Another example is the case of automobile exhaust emissions, which are usually reported in gm/mi. of hydrocarbon as methane--i.e., each carbon atom measured is assumed to have a molecular weight of 16 gm/mole. Evaporative emissions, on the other hand, are reported as straight mass, which means that a lower molecular weight is called for. Accounting for all carbon is further complicated by the fact that the procedures used to obtain automobile exhaust hydrocarbon estimates do not respond efficiently to all reactive species. Aldehydes, for example, are not often measured by standard procedures and must be added to the exhaust emissions estimates.

THE VOLUMETRIC EQUIVALENCE PRINCIPLE

The second important principle to remember when using the Carbon-Bond Mechanism is that the volumetric concentrations (in ppm) of most species used with the CBM are similar to both the volumetric measurements and the molar concentrations used in other mechanisms. One ppm of aromatic hydrocarbon bonds in the CBM is usually equivalent to 1 ppm of aromatic hydrocarbons in a lumped mechanism.*

We note two exceptions to the equivalence of speciation between the CBM and molecular mechanisms. The major exception is the PAR species, which includes not only the carbon in paraffinic molecules but also single-bonded carbon in other molecules. A molecule of propylene, for example, contains one single-bonded carbon in addition to the olefinic bond:



In other words, the CBM total reactive hydrocarbon (RHC) given in ppmC must equal

$$(OLE \times 2) + (ETH \times 2) + (ARO \times 6) + CARB + (DCRB \times 2) + PAR = RHC \text{ (in ppmC)} \quad .$$

SURROGATE CARBONYLS

A minor exception to the rule of equivalent speciation lies in the relationship of CARB as a reaction product to other species. Some compounds, especially internal olefins (e.g., trans-2-butene), react much more rapidly than do terminal olefins like propylene. Thus, instead of creating a new species with an atmospheric lifetime of only a few minutes, we chose to treat

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* This is not true, however, for "surrogate mechanisms" in which all hydrocarbons are assumed to be represented by some mixture of surrogate hydrocarbons (e.g., propylene and butane). Comparison of speciation in the CBM with that in a surrogate mechanism is obviously impossible.

internal olefins as if they had already reacted (i.e., as if an internal olefinic bond were already transformed to two carbonyls).

A similar approximation is used for cycloparaffins. No data exist for the reactions and reactivity rates of these compounds; however, we believe that they are more reactive than ordinary paraffinic hydrocarbons. At some point in the reaction scheme the ring structure must break, yielding two reactive sites instead of one. We therefore add one CARB group to the CBM splits for cycloparaffins to account for the extra reactive site.

SAMPLE CARBON-BOND CALCULATIONS

In appendix B we present the name, molecular weight, carbon number, and carbon-bond groupings for several compounds. This table can be referred to in the preparation of emission inventories for the Carbon-Bond Mechanism.

To show how the CBM bond groupings can be obtained for a variety of user objectives, we present several examples of such calculations. The first example is presented as Table 4.

Example 1

TABLE 4. CARBON-BOND GROUPINGS

Hydrocarbon Concentrations (ppm)		CBM Group/Molecule
Ethylene	1.051	1 ETH
Propylene	0.108	1 OLE + 1 PAR
Butane	1.13	4 PAR
trans-2-Butene	0.055	2 CARB + 2 PAR
2,3-Dimethylbutane	0.715	6 PAR
Toluene	0.121	1 ARO + 1 PAR
m-Xylene	0.108	1 ARO + 2 PAR
Formaldehyde	0.03	1 CARB

(continued)

Table 4

Carbon-Bond Calculations

ETH = 1 x 1.051 = 1.051

OLE = 1 x 0.108 = 0.108

ARO = (1 x 0.121) + (1 x 0.108) = 0.229

CARB = (2 x 0.055) + (1 x 0.03) = 0.14

PAR = (1 x 0.108) + (4 x 1.13) + (2 x 0.055)
+ (6 x 0.715) + (1 x 0.121) + (2 x 0.108) = 9.365

Source: University of California at Riverside Smog-Chamber Experiment (EC-231)

Example 2

Example 2 calculates the carbon-bond concentrations that would be used for the ambient hydrocarbon measurements reported by Kopczynski et al. (1972). Gas chromatographic analysis (GCA) accounted for 90 percent of total nonmethane hydrocarbons as identified by flame ionization analysis (FIA). Table 5(a) gives the carbon fraction allocated to each bond category for each molecular species as calculated from the bond-splitting information in appendix B. The calculated molar concentration for each bond group is also given. Table 5(b) gives the sum of each bond category as well as the carbon fraction for each bond category for the measured hydrocarbon mix. This information could be directly input to OZIPM, a computer program designed to generate EKMA-type isopleth diagrams with any kinetic mechanism.

Kopczynski et al. (1972) do not report carbonyl data for aldehydes or ketones. The response of aldehydes and ketones to FIA and GCA is inefficient. The carbon fraction shown for the CARB species in table 5(b) consists exclusively of surrogate carbonyls--compounds such as internal olefins (which form carbonyls rapidly); precise carbonyl data are lacking.

If the hydrocarbon splits in table 5(b) are used without correction for probable carbonyl concentrations, underprediction of the reactivity of the atmospheric mix results. Indeed, Kopczynski, Kuntz, and Bufalini (1975), prepared a "simulated Los Angeles mix" on the basis of measured concentrations in the 1972 study. They found that the simulated mix required the consumption

Example 2

TABLE 5. CARBON-BOND CONCENTRATIONS APPLIED TO AMBIENT HYDROCARBON MEASUREMENTS REPORTED BY KOPCZYNSKI ET AL. (1972)

(a) Carbon-Bond Concentrations in ppb

Measured Hydrocarbon	Carbon Fraction							Molar Concentrations					
Olefins	ppbC	ETH	OLE	ARO	PAR	CARB	NR	ETH	OLE	ARO	PAR	CARB	NR
Ethylene	151	1.0						75.5					
Propylene	60		0.67		0.33				20.0		20.0		
1-Butene | Isobutene	47		0.5		0.5				11.75		23.5		
trans-2-Butene | Methylacetylene	12*				0.25	0.25	0.5				3.0	3.0	6.0
cis-2-Butene	8				0.5	0.5						4.0	
1,3-Butadiene	11		0.5			0.5			2.75			5.5	
1-Pentene	11		0.4		0.6				2.2		6.6		
2-Methyl-1-butene	15		0.4		0.6				3.0		9.0		
trans-2-Pentene	22				0.6	0.4					13.2	8.8	
cis-2-Pentene	10				0.6	0.4					6.0	4.0	
2-Methyl-2-butene	29				0.6	0.4					17.4	11.6	
1-Hexene	15		0.33		0.67				2.5		10.0		
Unknown 7† | Unknown 8†	6 | 3	9	0.33		0.67				1.5		6.0		
Total	400							75.5	43.7		118.7	36.9	6.0

(continued)

TABLE 5

(a) (continued)

Measured Hydrocarbon	Carbon Fraction							Molar Concentrations					
Aromatics	ppbC	ETH	OLE	ARO	PAR	CARB	NR	ETH	OLE	ARO	PAR	CARB	NR
Toluene	271			0.86	0.14					38.7	38.7		
Ethylbenzene	67			0.75	0.25					8.4	16.75		
p-Xylene	100			0.75	0.25					12.5	25.0		
m-Xylene	215			0.75	0.25					26.9	53.75		
o-Xylene	87			0.75	0.25					10.9	21.75		
n-Propylbenzene	21			0.67	0.33					2.3	7.0		
m-Ethyltoluene p-Ethyltoluene	111			0.67	0.33					12.3	37.0		
tert-Butylbenzene o-Ethyltoluene	23			0.67	0.33					2.6	7.7		
sec-Butylbenzene 1,2,4-Trimethylbenzene	137*			0.63	0.37					14.4	50.5		
1,3,5-Trimethylbenzene	29			0.67	0.33								
Isopropylbenzene Styrene	76			0.7	0.22	0.074				8.9	17.0	5.6	
Total	1137									137.9	275.15	5.6	

(continued)

TABLE 5

(a) (continued)

Measured Hydrocarbon Paraffins	Carbon Fraction ppbC	ETH	OLE	ARO	PAR	CARB	NR	Molar Concentrations ETH	OLE	ARO	PAR	CARB	NR
Ethane	191				0.0								191.0
Propane	140				0.5						70.0		70.0
Isobutane	65				1.0						65.0		
n-Butane	286				1.0						286.0		
Isopentane	312				1.0						312.0		
n-Pentane	171				1.0						171.0		
Cyclopentane 2-Methylpentane	138*				0.91	0.09					125.6	12.4	
3-Methylpentane	68				1.0						68.0		
n-Hexane	82				1.0						82.0		
2,4-Dimethylpentane	89				1.0						89.0		
Cyclohexane	16				0.83	0.17					13.3	2.7	
3-Methylhexane	68				1.0						68.0		
n-Heptane	40				1.0						40.0		
Methylcyclohexane	49				0.86	0.14					42.1	6.9	
Unknown 1	6				1.0						6.0		
Unknown 2	11				1.0						11.0		
Unknown 3	37				1.0						37.0		
Unknown 4	28				1.0						28.0		
Unknown 5	23				1.0						23.0		
Unknown 6	80				1.0						80.0		
(Acetylene)	160				0.0								160.0
Total	2060										1617.0	22.0	

* Assume 50/50 split.

† Assume molecular weight of 6.

(continued)

TABLE 5

(b) Carbon-Bond Speciation Category*

Species	Σ Molar Concentrations (ppb)	Carbon Fraction	Normalized
ETH	75.5	0.042	0.048
OLE	43.7	0.024	0.027
ARO	137.9	0.23	0.26
PAR	2011.0	0.56	0.64
CARB	64.5	0.018	0.02
Non-Methane Nonreactive	427.0	0.119	

* Gas chromatograph accounted for 3597 ppbC (3170 ppbC RHC + 427 ppbC nonreactive). Flame ionization analysis (FIA): TNMHC = 4.0 ppmC (4000 ppb)

(c) Carbon-Bond Speciation Category Corrected for Unmeasured Hydrocarbons and Unmeasured Carbonyls

Species	Σ Molar Concentrations* (ppb)	Carbon Fraction Normalized †
ETH	$75.5 \times \frac{4000}{3597} = 84.0$	0.044
OLE	$43.7 \times \frac{4000}{3597} = 48.6$	0.025
ARO	$137.9 \times \frac{4000}{3597} = 153.4$	0.24
PAR	$2011.0 \times \frac{4000}{3597} = 2236.3$	0.58
CARB	$64.5 + 360.0^{\S} \times \frac{4000}{3597} = 431.7$	0.11

* Unmeasured reactive hydrocarbon = $(1 - \frac{3597 \text{ ppbC GCA}}{4000 \text{ ppbC FIA}}) = 10\%$

† Total reactive organic carbon = 3853.6 ppbC

§ Unmeasured carbonyl; see text

(concluded)

of 2.3 moles of carbon per mole of NO oxidized to NO_2 in a smog chamber. Kopczynski et al. (1972) found that samples of Los Angeles air required only 1.4 moles of carbon per mole of NO oxidized to NO_2. Kopczynski, Kuntz, and Bufalini (1975) suggested that other species, such as aldehydes, were contributing to NO oxidation in Los Angeles.

From these data we can estimate the CARB concentration necessary to replicate the oxidation reactivity observed by Kopczynski et al. (1972). If we multiply the molar bond concentrations shown in table 5(b) by the OH reaction-rate constant for each bond group, we obtain the production rate of peroxyl radicals (which oxidize NO to NO_2) from the measured hydrocarbons per OH concentration in the air sample:

Compound	Bond Concentration (ppm)	OH Reaction-Rate Constant ($ppm^{-1}min^{-1}$)	Peroxyl Radicals per OH Attack	Peroxyl Production Rate per OH (min^{-1})
ETH	0.0755	12,000	2	1,812
OLE	0.0437	37,000	2	3,234
ARO	0.1379	20,500	2	5,654
PAR	2.011	1,300	2.5*	6,536
CARB (surrogate)	0.0645	14,000	2	1,806
				19,042

* The "A factor" of 1.5 gives 1.5 $RO_2^{\cdot}$ + 1 $HO_2^{\cdot}$ per OH attack on a paraffinic bond.

The observed rate of peroxyl production was 2.3/1.4 = 1.64 times higher in the Los Angeles air sample than in the surrogate mix. Compounds unidentified by GCA for the Los Angeles air sample amounted to 10 percent of the total. If we make the conservative assumption that the unidentified compounds had the same reactivity as the identified mix, then the observed rate becomes 2.07/1.4 = 1.48 times higher than the laboratory mix. This adjustment for 10 percent unmeasured hydrocarbon raises all the calculated bond concentrations by 10 percent and increases the peroxyl production rate to 21160. min^{-1} per OH.

Given the observed "reactivity gap" of 0.48, we may estimate the concentration of carbonyl compounds necessary to account for the additional oxidation of NO to NO_2:

$$\frac{21160.\ \text{min}^{-1} \times 0.48}{14000\ \text{ppm}^{-1}\ \text{min}^{-1} \times 2} = 0.36\ \text{ppm (360 ppb)} \quad ,$$

which is equal to 9 percent of the observed hydrocarbon concentration and should be added to the carbon fractions shown in table 5(c).

Example 3

Example 3 also represents ambient sampling in the Los Angeles area (Calvert, 1976). In this case, however, the measurements are reported in molar units. To calculate CBM units from molar units, the appropriate bonds-per-molecule factor (from appendix B) is multiplied by the molar concentration.

Calvert (1976) stated that roughly 85 percent of total carbon atoms were detected as individual species. Thus about 0.58 ppmC remain unaccounted for in the analysis. If this excess carbon is reactive, we must make some assumption regarding its composition. Normalizing to total RHC (see table 6[b]) is equivalent to assuming that the composition of the unidentified carbon is similar to the average of that which was identified. This is what we did in the previous example. Alternatively, if we assume that the unidentified carbon is all paraffinic, the PAR fraction is then increased to 79 percent, and all other categories are reduced by 25 percent. Overall, the normalized carbon fractionation of RHC as shown in table 6(b) is the most conservative approach. However, it is important to bear in mind that only "surrogate carbonyls" are represented in this speciation. The reactivity calculations in example 2 indicate that this approach may underestimate the carbonyl component. We discuss this problem more thoroughly in section 5.

Example 4

Example 4 (Table 7) shows the correspondence between a molecular mechanism and the CBM as each would be used in the OZIPM program. In the OZIPM program two sets of numbers are input: the carbon number of each species and the carbon fraction of emissions represented by that species. In the case of the Carbon-Bond Mechanism, we also need to know the ethylene fraction of the olefinic emissions, because the CBM splits out ethylene from other olefins. This example is taken from a trajectory model study that uses the RAPS data base for St. Louis (Jeffries, 1981, private communication). For that study, ethylene was assumed to equal one-half of the olefinic emissions (internal olefins were ignored). Given that ethylene represents one-half of

Example 3

TABLE 6. LOS ANGELES AMBIENT MEASUREMENTS

(a) Reported in Molar Units

Compound	[RH], ppm Molar Basis	Bonds per Molecule x Concentration					
		NR	OLE	ETH	PAR	ARO	CARB
CH_4	2.01	2.01					
C_2H_6	0.049	0.049					
C_2H_4	0.043			0.043			
C_2H_2	0.038	0.038					
C_3H_8	0.037	0.0185			0.0185		
C_3H_6	0.0087		0.0087		0.0087		
iso-C_4H_{10}	0.012				0.048		
n-C_4H_{10}	0.037				0.148		
1-C_4H_8	0.0015		0.0015		0.0030		
iso-C_4H_8	0.0030		0.0030		0.0060		
iso-C_5H_{12}	0.0443				0.02215		
n-C_5H_{12}	0.0162				0.0810		
Cyclo-C_5H_{10}	0.0026				0.0104		0.0026
1-C_5H_{10}	0.004		0.004		0.016		
2-Methylbutene	0.0008				0.0032		0.0016
2,2-Dimethylbutene	0.0008				0.0032		0.0016
2-Methylpentane	0.0110				0.066		
3-Methylpentane	0.0100				0.06		
1-Hexene	0.0017		0.0017		0.0085		
n-Hexane	0.0100				0.06		
Cyclohexene	0.0107				0.0428		0.0214
2,2,3-Trimethylbutane	0.0077				0.0539		
C_6H_6	0.0082	0.0492					
2-Methylhexane	0.0069				0.0483		
3-Methylhexane	0.0063				0.0441		

(continued)

TABLE 6

(a) (continued)

Compound	[RH], ppm Molar Basis	Bonds per Molecule × Concentration					
		NR	OLE	ETH	PAR	ARO	CARB
1-Heptene	0.0044		0.0044		0.022		
$n\text{-}C_7H_{16}$	0.0043				0.0301		
Methylcyclohexane	0.0037				0.0222		0.0037
2,2,3- and 2,3,3-Trimethylpentane	0.0019				0.0152		
2,2,4-Trimethylpentane	0.0025				0.02		
Toluene	0.020				0.02	0.02	
1-Methylcyclohexene	0.0047				0.0235		0.0094
2,2,5-Trimethylhexane	0.0010				0.009		0.001
$n\text{-}C_8H_{18}$	0.0021				0.0168		
EtC_6H_5	0.0041				0.0082	0.0041	
p,m-Xylenes	0.014				0.028	0.014	
o-Xylene	0.0060				0.012	0.006	
$n\text{-}C_9H_{20}$	0.0013				0.0117		
$n\text{-}PrC_6H_5$	0.0010				0.003	0.001	
$sec\text{-}BuC_6H_5$	0.0050				0.02	0.005	
$n\text{-}C_{10}H_{22}$	0.0011				0.011		
$n\text{-}C_{11}H_{24}$	0.0010				0.011		
$n\text{-}C_{12}H_{26}$	0.0003				0.0036		
CO	1.91						
Total			0.0233	0.043	1.2384	0.0501	0.040

(b) Total RHC Normalized

Compound	RHC (ppm)	ppmC	Carbon Fraction of RHC
OLE	0.0233	0.0466	0.0271
ETH	0.043	0.086	0.0501
PAR	1.2347	1.2347	0.719
ARO	0.0501	0.306	0.178
CARB	0.044	0.044	0.0256
Total		1.7173	

(concluded)

Example 4

TABLE 7. COMPARISON OF MOLECULAR MECHANISM AND THE CBM AS USED IN THE OZIPM PROGRAM

OZIPM INPUTS		
Species	Average Carbon Number	Carbon Fraction of Emissions
Olefin*	3	0.193
Aromatic	8.1	0.142
Paraffin	6.0	0.601
Aldehyde	1	0.065

CARBON-BOND MECHANISM		
Olefin	2	2/6 x 1/2 x 0.193 = 0.032
Ethylene	2	1/2 x 0.193 = 0.0965
Aromatic	6	6/8.1 x 0.142 = 0.105
Aldehyde	1	0.065 = 0.065
Paraffin	1	(2/3 x 1/2 x 0.193) + 2.1/8.1 x 0.142 + 0.601 = 0.70

* Ethylene = one-half of the carbon in the olefin category.

the carbon in the olefin category, we can then calculate the average carbon number for the remaining olefinic compounds:

$$\text{carbon number} = \frac{\text{total carbon}}{\text{number of molecules}}$$

$$3 = \frac{0.193}{\underbrace{\frac{0.0965}{2}}_{\text{ethylene}} + \underbrace{\frac{0.0965}{x}}_{\text{other olefins}}}$$

$$\frac{3}{2} \cdot 0.0965 + \frac{3}{x} \cdot 0.0965 = 0.193 \quad ,$$

$$0.2895 = (0.193 - 0.14475)\, x \quad ,$$

$$6 = x \quad .$$

Thus, one-half of the olefinic carbon is ethylene (0.0965 of the total). Of the six carbon atom olefins remaining, one-third are olefinic bonds (two carbons per olefinic bond; six carbons per molecule). Thus the olefinic fraction is 2/6 x 1/2 x 0.193, or 0.032. The other calculations are straightforward: 6/8.1 of the aromatic molecules are aromatic bonds; the aldehydes do not change; and the remaining carbon is made up of PAR.

1 ppmC of emissions then equals:

0.032/2	ppm OLE
0.0965/2	ppm ETH
0.105/6	ppm ARO
0.065	ppm CARB
0.70	ppm PAR

We can also estimate olefin composition from the hydrocarbon data given in examples 2 and 3. From table 8 we see that olefinic carbon is composed of 37 percent ETH, 21 percent OLE, 12 percent internal olefins as CARB, and 30 percent PAR. Similarly, from examples 2 and 3 we estimate that 1.1 percent of primary paraffinic carbon can be placed in the CARB category because of the cyclic paraffins that are included.

TABLE 8. CARBON-BOND COMPOSITION OF OLEFINS

(Based on examples 2 and 3 in this chapter)

Species	Example 2	Example 3	Average
ETH	0.38	0.37	0.37
OLE	0.22	0.20	0.21
Internal olefin (CARB)	0.09	0.15	0.12
PAR	0.31	0.28	0.30
Average carbon number	2.9	2.8	2.86

These data indicate an average carbon number of nearly three, which agrees well with the estimate made on the basis of the RAPS emissions. Ethylene, however, appears equal to 40 percent, rather than 50 percent, of olefinic carbon.

If we use both the olefinic-composition factors in table 8 and the cyclic paraffin carbonyl surrogate for the OZIPM inputs, the CBM carbon splits become

$$OLE = 0.193 \times 0.21 = 0.0405,$$

$$ETH = 0.193 \times 0.37 = 0.0714,$$

$$CARB = 0.065 + (0.193 \times 0.12) + (0.011 \times 0.601) = 0.0948,$$

$$ARO = 0.142 \times 6/8.1 = 0.105,$$

$$PAR = (0.193 \times 0.3) + 2.1/8.1 \times (0.142) + (0.601 \times 0.989) = 0.689.$$

SECTION 5

HYDROCARBONS IN URBAN AREAS

In this section we review available data regarding the composition of hydrocarbons in polluted urban air. The study of ambient hydrocarbon composition and the related subject of speciation of pollutant emissions is important to the successful application of kinetic modeling of urban smog.

Any kinetic mechanism is liable to error if the various hydrocarbon species that it treats are improperly specified. This problem does not ordinarily arise in smog-chamber studies, because the experimenter has full control over the introduction of hydrocarbons into the reaction vessel. Nor does the speciation problem arise in the application of a surrogate mechanism such as that used in EKMA, where all hydrocarbons are assumed to be represented by a mixture of propylene and butane. The surrogate approach is inflexible, however, because it does not allow for the differences that do exist among hydrocarbon species.

Because a lumped-species mechanism like the Carbon-Bond Mechanism is more flexible than a surrogate mechanism, there is greater potential for error. An "assumed hydrocarbon speciation" can be supplied for the CBM to set exact proportions for the emitted hydrocarbon species, thereby eliminating the flexibility of the modeling exercise. Instead, we prefer to present information about the probable composition of hydrocarbons within urban areas. Such data allow the user to judge whether or not a particular emissions inventory lies within the limits of variation for hydrocarbon composition. At the end of this section, we provide a default hydrocarbon composition profile, which can be used in the absence of data or when the modeler suspects an error in the speciation data.

HYDROCARBON SPECIATION FOR THE LOS ANGELES AREA

Killus et al. (1980) prepared estimates of hydrocarbon composition for the Los Angeles area on the basis of the work of Trijonis and Arledge (1975). It should be noted that these estimates, shown in table 9, were prepared prior to the adoption of the methodology in which internal olefins and a fraction of cyclic paraffins are treated as carbonyl emissions. This

TABLE 9. HYDROCARBON EMISSIONS IN THE LOS ANGELES BASIN BY CARBON FRACTION IN CATEGORIES USED IN THE SAI URBAN AIRSHED MODEL

Source Category	Percentage of Total Hydrocarbon Emissions	Carbon Fraction					
		Olefins*	Paraffins	Ethylene	Aromatics	Carbonyls†	Nonreactive Hydrocarbons
Land motor vehicles†	67.5	0.032	0.61	0.032	0.235	0.037	0.091
Aircraft	1.6	0.073	0.64	0.038	0.163	0.058	0.09
Refineries	1.9	0.04	0.84	0.0	0.17	0.0	0.05
Other	29.0	0.026	0.565	0.016	0.066	0.011	0.326
Total hydrocarbons from all sources	--	0.029	0.60	0.027	0.182	0.029	0.158
Normalized carbon fraction emissions excluding nonreactive HC	--	0.034	0.71	0.032	0.22	0.034	
Normalized carbon fractions with "surrogate" carbonyls	--	0.024	0.70	0.032	0.22	0.055	

* Olefirs excluding ethylene.

† Carbonyl emissions are estimates only (because they would not have been detected by the measurement methods used); thus the sum of the weight fractions in this row is greater than 1.

"surrogate carbonyl" approximation tends to reduce slightly the olefinic and paraffinic bond groups and to increase the carbonyl emissions. Internal olefins represent between 10 and 15 percent of the carbon in olefin molecules, which is 30 to 40 percent of OLE (as shown in section 4). Additional surrogate carbonyls represent about 1 percent of the remaining emissions. Table 9 also shows the principal effect of the "surrogate carbonyl" approximation--the reduction of olefins to 0.024 of the RHC emissions and the increase of carbonyls to 0.055 of RHC.

The Los Angeles inventory of volatile organic carbon emissions, as used in the SAI Airshed Model, is presently undergoing review and modification (Allen, 1981, private communication). The most recent emissions splits (obtained by application of correction factors to the summation of the emissions data file for the Airshed Model) are given in table 10.

Hydrocarbon speciation for the motor-vehicle emissions shown in table 10 is taken from measurements made by Black and High (1980) for an uncontrolled automobile burning fuel that contains 22 percent aromatics (17 percent in carbon-bond units). However, the average aromatic content measured by Mayrsohn and Crabtree (1976) in a sample of Los Angeles gasolines was 37 percent (26 percent in carbon-bond units). Such speciation for gasoline corresponds well with the measurements made by Kopczynski et al. (1972) [described in example 2 in section 4] in which the aromatic-bond fraction was greater than 20 percent. However, Calvert (1976) [example 3 in section 4] reported hydrocarbon composition estimates in which the aromatic-bond fraction was only 17 percent. The estimates made by Calvert were derived from typical data from the LARPP study in Los Angeles. Thus, the range of emissions estimates for the Los Angeles area is corroborated to some extent by atmospheric measurements (see table 11).

HYDROCARBON SPECIATION FOR OTHER URBAN AREAS

Table 12 presents data regarding hydrocarbon speciation for several urban areas (Kopczynski et al., 1975). Table 13 indicates the carbon-bond composition for these samples, using the carbon-composition factors outlined in example 4 in section 4. Note that CARB contains "surrogate carbonyl" only. Actual carbonyl concentrations are likely to be higher than what is indicated by these data.

Table 14 presents the data from a study performed by Ferman, Eisinger, and Monson (1977) for the Denver area. The sampling site was 6 km northwest of downtown Denver, and as the table indicates, the fractions for ethylene, olefins, and aromatics are all two-thirds of those derived from the Kopczynski et al. data for a Denver expressway. Surrogate carbonyl for the off-highway data represents an even smaller fraction (relative to the expressway data)

TABLE 10. LOS ANGELES EMISSIONS SPECIATION FOR 1974 EMISSIONS INVENTORY

Source	OLE	PAR	ETH	ARO	CARB
Land motor vehicles	0.1	0.59	0.124	0.19	0.046
All sources	0.049	0.705	0.090	0.154	0.046

Source: California ARB (1981).

TABLE 11. CARBON-BOND FRACTIONS OF RHC FOR EMISSIONS AND AMBIENT MEASUREMENTS IN THE LOS ANGELES AREA

Estimate or Measurement	OLE	PAR	ETH	ARO	CARB
Emissions estimates for 1974					
Killus et al. (1980)	0.024	0.7	0.032	0.22	0.055
California ARB (1981)	0.049	0.705	0.096	0.154	0.039
Atmospheric measurements					
Kopczynski et al. (1972)	0.027	0.64	0.048	0.26	0.07*
Calvert (1976) (LARPP--1974)	0.027	0.72	0.05	0.18	0.026†

* Calculated from excess reactivity over laboratory surrogate mix (see Example 2 in section 4).

† Surrogate CARB only; aldehydes and ketones not measured.

TABLE 12. RATIOS OF POLLUTANTS TO SUM OF HYDROCARBONS LESS C_1 TO C_3 PARAFFINS IN ROADWAY SAMPLES

Pollutant	St. Louis, 1972 Highways	St. Louis, 1972 Downtown	Denver Expressway Interchange 1971	L.A. Underpass 1970	Lincoln Tunnel 1970
C_3 + paraffins	0.42	0.50	0.57	0.41	0.46
Olefins	0.23	0.19	0.15	0.13	0.22
C_6 + aromatics	0.25	0.23	0.23	0.41	0.26
Acetylene	0.068	0.068	0.056	0.053	0.067
Carbon monoxide	5.0	5.1	4.0	3.2	4.5
Nitrogen oxides	0.13	0.22	0.16	0.14	0.40

Source: Kopczynski, Kuntz, and Bufalini (1975)

TABLE 13. URBAN HYDROCARBON COMPOSITION DATA

(a) Carbon-Bond Splits for Data in Table 12

Site	From Olefins				From ARO		From PAR		Total
	ETH	OLE	CARB	PAR	ARO	PAR	PAR	CARB	PAR
St. Louis Highways	0.085	0.048	0.028	0.069	0.19	0.06	0.404	0.006	0.533
Downtown	0.07	0.04	0.023	0.057	0.15	0.04	0.493	0.007	0.59
Denver Expressway	0.056	0.0315	0.018	0.045	0.15	0.04	0.562	0.008	0.65
Los Angeles Underpass	0.048	0.027	0.016	0.039	0.31	0.10	0.404	0.006	0.54
Lincoln Tunnel	0.08	0.046	0.026	0.066	0.20	0.06	0.453	0.007	0.58

(b) Normalized to 100 Percent Carbon

Site	ETH	OLE	PAR	ARO	CARB
St. Louis Highways	0.094	0.053	0.59	0.21	0.038
Downtown	0.076	0.044	0.64	0.16	0.033
Denver Expressway	0.059	0.033	0.68	0.16	0.027
Los Angeles Underpass	0.05	0.028	0.57	0.33	0.023
Lincoln Tunnel	0.085	0.049	0.62	0.21	0.035

TABLE 14. STATISTICAL SUMMARY OF HYDROCARBON DATA FOR THE DENVER AREA*

(a) Hydrocarbon Concentrations (ppbC)

Hydrocarbon	Average	99th Percentile	Maximum
Ethane†	69	447	638
Ethylene	53	304	508
Acetylene†	59	344	530
Propane†	95	785	924
Propylene	25	146	243
Isobutane	58	557	857
n-Butane	123	685	979
Isopentane	111	600	999
n-Pentane	68	586	781
2-Methylpentane	53	424	652
3-Methylpentane	37	254	509
n-Hexane	55	321	535
2,2,3-Trimethylbutane	32	218	485
Cyclohexane	17	164	547
Benzene†	18	116	178
2-Methylhexane	34	198	441
3-Methylhexane	38	240	481
1-Heptene	20	135	301
n-Heptane	33	210	420
Methylcyclohexane	28	177	272
Toluene	64	338	520
1-Methylcyclohexane	23	120	239
n-Octane	22	153	766
Ethylbenzene	15	80	115
m- and p-Xylene	47	260	372
o-Xylene	24	142	571
n-Nonane	19	116	334
sec-Butylbenzene	30	167	419
n-Decane	22	146	209
n-Undecane	14	84	120
Total	1112	7333	

* Based on >500 points for each compound. Compounds listed are the 30 with the highest average concentrations. Minimum concentrations for all are less than 1 ppbC.

† Nonreactive (propane 0.5 reactive).

(continued)

TABLE 14

(b) Carbon-Bond Fractions for Denver Hydrocarbon Data

	ETH	OLE	CARB	ARO	PAR
Average	0.0476	0.02	0.009	0.123	0.80
99th Percentile	0.0415	0.0185	0.0095	0.1025	0.83

(concluded)

apparently because of the exclusion of trace compounds like internal olefins. These data represent the least reactive mix of hydrocarbons in any data set that we have analyzed. Use of fractions lower than these for ethylene, olefins, and aromatics is not recommended. Because carbonyl concentrations are usually unmeasured and conjectural, we present later in the section some carbonyl emissions estimates.

Table 15 gives hydrocarbon-composition data for sites in the eastern United States and the carbon-bond fractions calculated from these data. Since no internal olefins were reported and only a small quantity of cyclic paraffins was measured, no fraction of surrogate CARB is calculated. Note also that the fraction of ethylene as carbon in olefin molecules varies from 0.33 to 0.49, with an average of 0.41. This figure is similar to the 0.37 fraction that we have used in the preceding examples.

The data in table 16 are derived from samples taken in September 1973 by Lonneman and Bufalini (private communication) for the Houston, Texas, area. The high ethylene fraction calculated for these samples represents the major discrepancy between them and samples taken from other urban areas. The ethylene concentrations observed were in some cases three to five times the acetylene concentration, which indicates a large nonautomotive source of ethylene in the Houston area. Other data gathered in Houston (Lonneman and Bufalini, private communication; Siddiqi and Worley, 1975) show more common ethylene fractions, with approximately a one-to-one ratio to acetylene.

CARBONYL COMPOUNDS IN URBAN AIR

In our discussion of hydrocarbon composition thus far, we have not included carbonyl compounds per se. Because aldehydes and ketones require special measurement techniques, they are not included in the available composition data, and only "surrogate carbonyl" can be reported. However, the photochemical reactivity observed in urban air pollution leads to the conclusion that significant concentrations of carbonyl compounds do exist in urban atmospheres, both as primary emissions and as secondary reaction products.

In the following subsection we discuss the importance of carbonyl compounds in the formation of smog, and we then examine some estimates of carbonyls in emissions and ambient air.

RADICAL SOURCES AND HYDROCARBON REACTIVITY

Smog formation results from the catalytic oxidation of hydrocarbons by hydroxyl radicals (OH). The concentration of hydroxyl radicals in the

TABLE 15. HYDROCARBON COMPOSITION DATA FOR SELECTED SITES IN THE EASTERN UNITED STATES

(a) Ratio* of Sum of Paraffins, Olefins, and Aromatics to Acetylene at New York-New Jersey Station at All Times

Component	Bayonne	Linden	Manhattan	Brooklyn	Lincoln Tunnel
$\sum$ Paraffins	19.50	19.08	8.51	11.29	6.81
$\sum$ C_4 paraffins	5.34	5.24	1.97	2.47	1.41
$\sum$ C_5 paraffins	6.48	5.65	2.89	3.21	1.90
$\sum$ Olefins	4.83	5.75	2.21	2.97	3.24
$\sum$ C_4 olefins	0.99	1.35	0.39	0.50	0.59
$\sum$ C_6 olefins	0.11	0.14	0.05	0.05	0.08
$\sum$ Aromatics	12.77	11.70	6.74	11.3	3.87
Toluene	5.20	4.84	2.16	4.77	1.27
$\sum$ C_8 aromatics	5.89	4.87	2.67	4.67	1.44
$\sum$ C_9 + C_{10} aromatics	1.68	1.99	1.91	1.86	1.16
Ethylene	1.83	1.91	1.08	1.28	1.33
Propylene	0.54	0.87	0.31	0.38	0.61
Average acetylene concentration, ppb carbon	15.9	21.7	43.7	32.1	
Total	37.1	36.5	17.46	25.56	13.92

Source: Lonneman et al. (1974)

(continued)

TABLE 15

(b) Average Ratios* of Hydrocarbon to Acetylene in Lincoln Tunnel

Component	Ratio of Component to C_2H_2 and Standard Deviation
Ethylene	1.33 ± 0.14
Isobutane	0.34 ± 0.05
n-Butane	0.97 ± 0.12
Propylene	0.61 ± 0.07
Isopentane	1.25 ± 0.14
Isobutylene	0.34 ± 0.04
Butene-1	
Sum of C_4 olefins	0.60 ± 0.07
n-Pentane	0.62 ± 0.07
Sum of C_5 olefins	0.53 ± 0.08
Cyclopentane	0.76 ± 0.08
2-Methylpentane	
3-Methylpentane	0.34 ± 0.04
n-Hexane	0.36 ± 0.05
2,4-Dimethylpentane	0.34 ± 0.04
2,2,4-Trimethylpentane	0.27 ± 0.23
Toluene	1.27 ± 0.23
Ethyl benzene	0.22 ± 0.03
p-Xylene	0.25 ± 0.03
m-Xylene	0.70 ± 0.15
o-Xylene	0.28 ± 0.04
Sum of C_8 aromatics	1.44 ± 0.25
3 & 4-Ethyl toluene	0.38 ± 0.05
sec-Butyl benzene	0.40 ± 0.06
1,2,4-Trimethyl benzene	
Sum of paraffins	6.81 ± 0.92
Sum of olefins†	3.24 ± 0.32
Sum of aromatics	3.87 ± 0.58
Total nonmethane hydrocarbons	13.9 ± 1.5
Carbon monoxide	63.4 ± 6.1

* Ratios were calculated from component concentrations in parts-per-billion carbon.

† Average carbon number for olefins = 2.88
Ethylene = $\sum$ olefin x 0.41.

(continued)

TABLE 15

(c) Carbon-Bond Fractions for Data Presented in Table 15(a) and (b)

Site	ETH	OLE	ARO	PAR	CARB
Bayonne	0.049	0.0405	0.268	0.64	--
Linden	0.052	0.057	0.248	0.64	--
Manhattan	0.062	0.026	0.29	0.62	--
Brooklyn	0.0501	0.03	0.18	0.74	--
Lincoln Tunnel	0.0955	0.066	0.208	0.63	--

(concluded)

TABLE 16. COMPOSITION OF HYDROCARBON IN HOUSTON AIR

	Fraction of Carbon per Bond Category					
Site	ETH	OLE	PAR	ARO	Surrogate CARB	Nonreactive
H01	0.11	0.022	0.43	0.2	0.016	0.22
	0.14	0.028	0.55	0.26	0.02	--
H05	0.107	0.057	0.57	0.16	0.026	0.08
	0.12	0.062	0.62	0.17	0.0285	--

atmosphere is small (about 10^{-7} ppm), but because they are rapidly destroyed, a constant influx of such radicals is necessary to maintain the smog-formation process. Most of the radicals necessary to generate smog are formed by the photolysis of oxygenated hydrocarbons--e.g.:

$$HCHO + h\upsilon \xrightarrow{+O_2} CO + HO_2 + HO_2 \quad ,$$

followed by

$$HO_2 + NO \rightarrow NO_2 + OH \quad .$$

Since photolyzable oxygenates are intermediate products of the process of hydrocarbon oxidation, the smog process is self-perpetuating; however, under some circumstances, it is not self-starting. If a pure hydrocarbon of relatively low reactivity were to be irradiated in an atmosphere free of extraneous sources of radicals, the smog-formation process would never be initiated. Urban air, however, contains numerous initial radical sources. Some oxygenated hydrocarbons are formed in the combustion process, and others are formed when extremely reactive hydrocarbons (like trans-2-butene) are exposed to a background of trace ozone. This process represents one of the sources of "surrogate carbonyl" used in the CBM. Inorganic radical sources are also important in the formation of oxygenated hydrocarbons. Perhaps the most important source for the troposphere is the photolysis of ozone:

$$O_3 + h\upsilon \rightarrow O^1D + O_2 \quad ,$$

$$O^1D + H_2O \rightarrow OH + OH \quad .$$

This process dominates in clean air in which the concentration of hydrocarbons and nitrogen oxides is low.

In urban or industrial areas where the concentration of nitrogen oxides and nitrates is high, nitrous acid (HONO) photolysis can play an important role in smog formation:

$$HONO + h\upsilon \rightarrow H + NO \quad .$$

Nitrous acid, which has been observed in urban air, may be a minor component of automobile exhaust. It can be formed in liquid water droplets (Schwartz and White, 1981) or as part of the denitrification process in vegetation (Anderson et al., 1978).

HONO has been detected in urban air at night near Riverside, California (Platt, et al., 1980) at concentrations of 3 percent to 6 percent of ambient

NO_2. Presumably, HONO is formed in heterogeneous reactions near the emissions source of NO_x, in this case automotive exhaust (the sample path in the Riverside study included a section of a freeway). HONO has been observed in direct sampling of auto exhaust under some conditions (Winer, 1981, private communication).

Although total NO_x was not reported in the study of Platt et al., NO_2 concentrations are typically one-third of total NO_x in the Los Angeles and San Gabriel basin area (LAAPCD, 1974, Hayes, private communication). This would put emissions of HONO in the range of 1 to 2 percent of total NO_x. In our kinetic simulation studies (Whitten et al., 1979; Whitten, Killus, and Hogo, 1980), we have found that one-third of the equilibrium concentration of HONO (calculated from the concentrations of NO, NO_2, and water vapor) is generally sufficient to explain initiation phenomena in smog-chamber experiments. For a NO_2-to-NO_x ratio of 0.33 and a water vapor concentration of 15,000 ppm, this calculated concentration of HONO equals 1.9 percent--excellent agreement with the atmospheric measurements.

In modeling urban air, one might wish to include the effects of HONO by including the species and specifying its emissions as approximately 2 percent of NO_x. However, as mentioned previously, for atmospheric studies the Carbon-Bond Mechanism is usually implemented without the chemistry of HONO. Except for the initiation effects discussed earlier, nitrous acid chemistry has a negligible effect on the calculations.

We have devised a methodology to simulate the effects of HONO emissions by specifying an emission of DCRB, the highly photolytic dicarbonyl species. DCRB has a photolysis rate that is nearly as high as that of HONO. Since the radical yield for DCRB photolysis is twice that of HONO, the emissions rate of DCRB should be only 1 percent that of NO_x, one-half the assumed HONO emissions rate. Although DCRB emits peroxyl rather than hydroxyl radicals, the peroxyl radicals are rapidly converted to OH by reaction with NO. The excess NO-to-NO_2 conversions produced by this approach amount to only a few percent of total NO_x, and the discrepancy in carbon-mass balance is less than 1 percent.

EMISSIONS OF CARBONYL COMPOUNDS

In addition to their role in the initiation of the smog process, carbonyl compounds are also of major importance to smog chemistry, because a significant fraction of hydrocarbon reactivity* results from the oxidation of carbonyl compounds by the hydroxyl radical. In section 4, when we compared

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* The term "reactivity" has acquired a variety of meanings in smog chemistry. In this context we define it as the oxidative production of peroxyl radicals, a process which then effects a conversion of NO to NO_2.

the reactivity rate of an urban air sample with that of a surrogate laboratory smog mixture containing pure hydrocarbons, we found the reactivity rate for the urban air sample to be about 40 percent greater than that of the surrogate. Furthermore, since carbonyls are a principal reaction product of hydrocarbons, a significant fraction of the peroxyl radicals formed in the laboratory hydrocarbon mixture results from the oxidation of carbonyls.

The Carbon-Bond Mechanism is designed to treat explicitly the carbonyl oxidation products of hydrocarbons. However, primary emissions make up a significant fraction of carbonyl compounds, and unless the emissions inventory of such compounds is reasonable, no mechanism, however well designed, will produce acceptable results. Thus, the modeler must have an understanding of the range of plausible values for the carbonyl composition of urban volatile organic compounds.

Dimitriades and Wesson (1972) reviewed available information concerning the relative levels of aldehydes and hydrocarbons found in automobile exhaust. In tests performed by the U.S. Bureau of Mines (Sawicki, Stanley, and Elbert, 1961; Dimitriades and Wesson, 1972), a mole fraction of total aldehyde per mole of hydrocarbon was calculated to range from 0.06 to 0.09. Other studies indicated greater variation, with mole fractions of aldehyde ranging from 0.07 to 0.35 (Oberdorfer, 1967) and from 0.12 to 0.20 (Wadowski and Weaver, 1970). Dimitriades and Wesson (1972) concluded that total aldehyde levels in pre-1970 auto exhaust represented about 10 percent of total hydrocarbon on a molar basis and 5 percent on a carbon basis (the aldehydes being about 60 percent formaldehyde on a molar basis).

Altshuller and McPherson (1963) measured ambient concentrations of formaldehyde and acrolein. Acrolein was found to make up 10 percent to 15 percent of the concentration of formaldehyde, thus indicating the probable importance of carbonyl species other than simple aldehydes. Seizinger and Dimitriades (1972) identified numerous carbonyl compounds in automobile exhaust--notably acrolein, acetone, and the aromatic aldehydes. Although Altshuller and McPherson (1963) did not report aldehydes as a fraction of reactive hydrocarbon, the formaldehyde concentrations observed (0.01 to 0.115 ppm) were consistent with the 5 percent carbon fraction suggested by Dimitriades and Wesson (1972).

In an analysis of monitoring data for the Los Angeles area (Scott Research Laboratories, 1970), Killus et al. (1980) concluded that aldehyde emissions were similar to olefin emissions when calculated on a molar basis. If this assumption is made, the data given in this chapter indicate aldehyde emissions that range from 0.034 to 0.074 as a fraction of emitted reactive carbon.

Data are very sparse for emissions from vehicles having pollution-control devices. However, in a review of recent data, Bulon, Malko, and Taback (1978) found no major differences in the formaldehyde emissions from controlled and uncontrolled vehicles. Reported emission levels were fairly low in these studies: approximately 2 to 3 percent of total RHC. Note that total aldehyde emissions would be expected to be higher and total carbonyls higher still.

The preceding analysis provides an outline of plausible carbonyl emissions in an urban emissions inventory. Formaldehyde emissions alone account for perhaps 2 to 6 percent of the carbon emitted in automobile exhaust; however, formaldehyde would account for only 1 to 4 percent of total emitted reactive carbon, since other emission processes (e.g., evaporation) seldom emit aldehydes per se.

Adding other aldehydes to formaldehyde increases our estimate of carbonyl emissions by approximately 50 percent (since formaldehyde represents 60 percent of aldehyde emissions on a molar basis). The addition of other carbonyl compounds (e.g., acetone, acrolein, and benzaldehyde) increases the carbonyl emissions rate still further, to perhaps twice that of emitted formaldehyde. Finally, surrogate carbonyl in the CBM accounts for perhaps 2 percent of emitted carbon.

In the CBM, carbonyl emissions as a fraction of total reactive carbon emissions would be expected to represent a minimum of 5 percent, which is in agreement with the assumptions used in other mechanisms (e.g., EKMA). Total aldehyde emissions could be as high as 7 percent and total carbonyls as high as 10 percent of reactive carbon (on the basis of reactivity differentials between urban air and laboratory surrogate mixes) [see example 2, section 4]. With the onset of photochemical smog formation, the carbonyl fraction increases because of oxidation of reactive hydrocarbons to aldehydes, ketones, glyoxals, and so forth. This process eventually reaches a photochemical equilibrium in which carbonyl carbon can represent as much as 25 percent of reactive carbon.

SUMMARY OF URBAN HYDROCARBON COMPOSITION

In this section we have presented a variety of hydrocarbon-composition data reported in carbon-bond units. Since the CBM allows for easy inventory of emissions, ambient data, and modeled concentrations, the ranges of composition data can be used to ascertain whether a particular modeling study is employing a realistic hydrocarbon composition. Ranges are presented in table 17, and a recommended composition is indicated for those studies in which detailed species data are lacking.

TABLE 17. RANGES OF URBAN HYDROCARBON COMPOSITION

(Fractions Normalized to RHC)

Compound	Carbon Fraction	
	Range	Recommended
ETH	0.03 → 0.12	0.05
OLE	0.02 → 0.06	0.03
ARO	0.10 → 0.33	0.22
PAR	0.55 → 0.80	0.65
CARB*	0.03 → 0.11	0.05

* Includes surrogate carbonyl from internal olefins and cyclic paraffins.

SECTION 6

SUMMARY

The original publication of the Carbon-Bond Mechanism (CBM-1, given in Whitten, Hogo, and Killus, 1980) introduced the concept of treating the atmospheric chemistry of complex mixtures of organic molecules as if the carbon atoms reacted more or less independently according to their local bonding. Since that introduction, the mechanism has undergone two major updates, and considerable experience with its use in atmospheric models has shown that proper use of the mechanism is essential to produce good results. This report presents the latest version of the Carbon-Bond Mechanism (CBM-III) in section 1, followed by a guide to using virtually any version of the CBM in section 2. In section 3, which also concerns the use of the CBM, specific urban reactivities are illustrated and a recommended set of CBM fractions to represent urban organics is developed for cases where data are lacking (table 17).

The latest CBM update, given in section 1, is mainly concerned with the chemistry of aromatics. Dicarbonyl compounds and nitroaromatic compounds have been shown to play a significant role in the smog chemistry of aromatics. Reactions have therefore been introduced into CBM-III to account for similar reactions identified in the detailed or explicit chemistry of aromatics, especially toluene. The CBM update also includes changes in several rate constants to reflect recent independent measurements and evaluations. Finally, some minor changes in handling ketones have been introduced.

Section 2 explains how the CBM shows key advantages over other mechanisms in actual use. For instance, the averaging of molecular weights is eliminated; carbon conservation is automatic; reactivity averaging is often done over a narrow range; molecules with various functional groups can be handled in a straightforward manner; and the CBM concept tends to work best for complex mixtures, although adjustments can be made to treat individual hydrocarbons. Important principles relating to successful applications of the CBM are also discussed. Some of these principles are the accounting of all reactive carbon, the volumetric equivalence between CBM units and molecular concentrations of certain species, and the surrogate nature of the CBM carbonyl species. Examples of converting specific molecular information into CBM speciation are then presented.

Section 3 has been included to show how proper speciation can be developed for several urban areas. Although the CBM has been formulated to respond correctly to changes in reactivities, this sensitivity can lead to incorrect results if the CBM is improperly utilized. In particular, the CBM is very sensitive to carbonyl levels. A review of some available data is presented. Finally, a set of CBM fractions representative of typical urban reactivity is presented for use in the absence of speciation data. If speciation data appear to give quite different CBM fractions than this representative set, then the data should be checked to ensure that the differences can be explained.

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Appendix A

VALIDATION SIMULATIONS FOR CARBON-BOND MECHANISM III

UNIVERSITY OF CALIFORNIA AT RIVERSIDE--SEVEN COMPONENT RUNS

One of the requirements of a kinetic mechanism is that it respond appropriately to changes in hydrocarbon composition. Three different hydrocarbon mixtures containing varying amounts of olefins, paraffins, and aromatics were used in the eleven modeling experiments performed at UCR (see table A-1). As can be seen from the simulation results shown in figures A-1 through A-11, CBM-III gives reasonable results for all three mixtures of hydrocarbons.

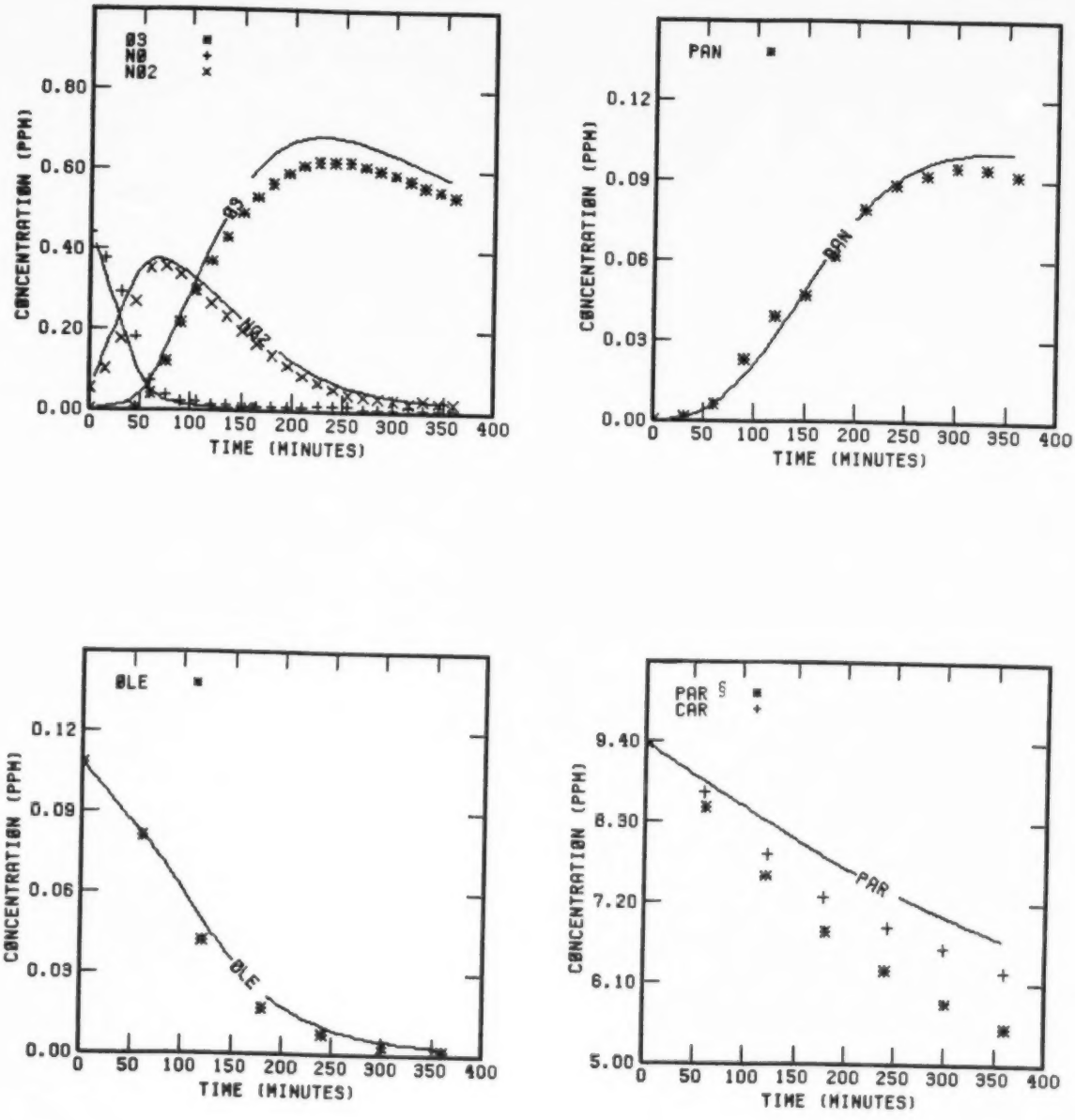
Simulations more accurate than those we have presented can be achieved by adapting CBM-III to the specific hydrocarbons in these experiments rather than using the default values for various rate constants. For example, the mixture of butane and 2,3-dimethylbutane in the paraffin component has an average reaction rate with OH of approximately 1100 $ppm^{-1}min^{-1}$, which is lower than the default value of 1300 $ppm^{-1}min^{-1}$. Similarly, the default speciation of CARB in CBM-III is one-half formaldehyde, one-quarter higher aldehydes, and one-quarter ketones. The actual measured carbonyl compositions in these experiments varied from these ratios.

The only variable factor for each experiment was the initial concentration of HONO that was assumed to be formed when the chamber was loaded with NO_x. These concentrations are given in table A-1. Initial HONO varies from 0 to 12 ppb. The maximum HONO used is 2.5 percent of NO_x, which is similar to the ratios of HONO to NO_2 that have been observed in the atmosphere (Platt et al., 1979).

TABLE A-1. INITIAL CONDITIONS AND REACTIVITY DATA FOR SEVEN HYDROCARBON/NO_x EXPERIMENTS

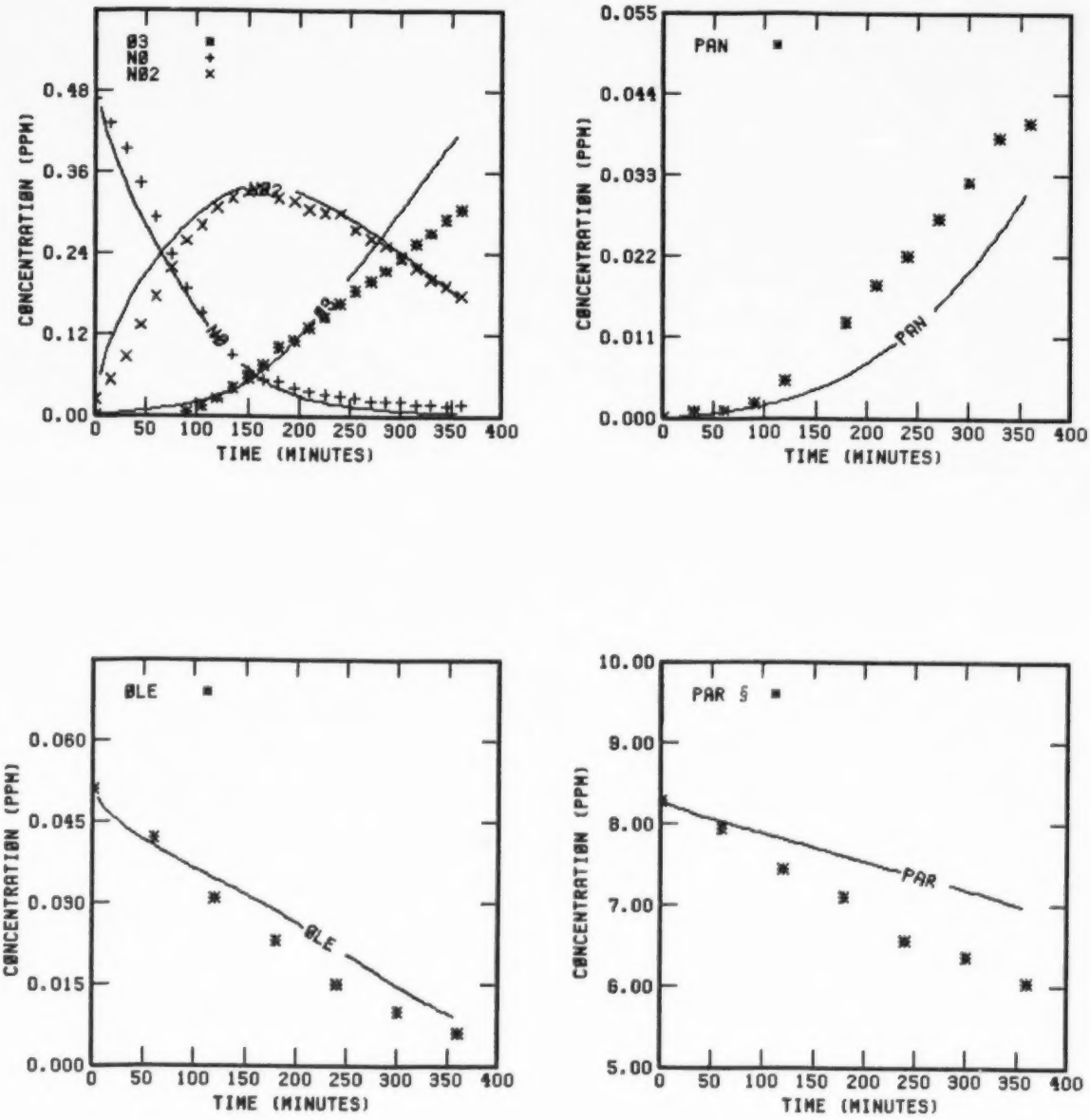
	Concentration (ppm)										
EC Run No.	231	232	233	237	238	241	242	243	245	246	247
EPA Run No.	4	1	2	4	3	5	7	7A	6	1	8
Mixture	B	A	A	B	B	B	C		C	A	C
Reactant											
Ethene	1.051	0.258	0.260	0.875	0.982	0.484	2.014	1.9[illegible]	2.055	0.253	1.025
Propene	0.108	0.051	0.051	0.100	0.093	0.045	0.109	0.109	0.104	0.049	0.054
trans-2-Butene*	0.055	0.026	0.025	0.050	0.047	0.024	0.108	0.110	0.102	0.026	0.053
n-Butane	1.130	1.102	1.085	1.025	0.966	0.464	0.558	0.568	0.534	1.058	0.273
2,3-Dimethylbutane	0.715	0.612	0.648	0.463	0.420	0.211	0.203	0.084	0.185	0.538	0.080
Toluene	0.121	0.032	0.034	0.086	0.083	0.040	0.306	0.155	0.321	0.023	0.145
m-Xylene	0.108	0.029	0.033	0.091	0.084	0.044	0.306	0.154	0.317	0.023	0.145
Total HC (ppmC)	13.17	9.31	9.50	10.46	10.07	4.95	12.82	9.74	12.86	8.56	6.17
NO	0.440	0.469	0.096	0.377	0.718	0.379	0.377	0.386	0.743	0.386	0.380
NO_2	0.052	0.024	0.007	0.106	0.234	0.110	0.125	0.114	0.259	0.122	0.125
NO_x	0.492	0.492	0.103	0.483	0.952	0.489	0.503	0.502	0.992	0.506	0.505
HONO	0.006	0.004	0.004	0.008	0.010	0.008	0.010	0.010	0.020	0.012	0.010
HCHO	0.020	0.009	0.004	0.0	0.026	0.018	0.028	0.0	0.016	0.000	0.003
Reactivity											
NO_2 max (ppm)	0.357	0.333	0.071	0.368	0.663	0.351	0.400	0.394	0.752	0.366	0.369
at time (min)	75	150-165	30-45	60	120	135	30	30	60	135	60
O_3 max (ppm)	0.623	--	0.330	0.655	0.692	--	0.682	0.716	0.892	0.574	0.657
at time (min)	225-255	--	240-345	240	435	--	105	135	180	570	210-240
6-hr O_3 (ppm)	0.540	0.305	0.325	0.584	0.674	0.408	0.418	0.711	0.635	0.374	--
PAN max (ppm)	0.095	--	0.307	0.100	0.113	--	0.140	0.100	0.194	0.070	0.106
at time (min)	270-330	--	300	300	495	--	180	135-150	240	570	300
6-hr PAN (ppm)	0.092	0.040	0.036	0.098	0.084	0.047	0.111	0.100	0.162	0.041	--
Physical Parameters (Averages)											
Temperature (°F)	85.3	85.3	85.0	86.2	86.8	86.5	86.0	85.0	86.3	86.5	86.4
RH (%)	42.5	54.0	53.0	57.0	59.5	50.5	60.5	54.5	50.5	53.0	54.0
Radiometer (mv)	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.23

* In the Carbon-Bond Mechanism, internal olefins are treated as two carbonyl groups, i.e., their reaction times are asumed to be instantaneously fast.



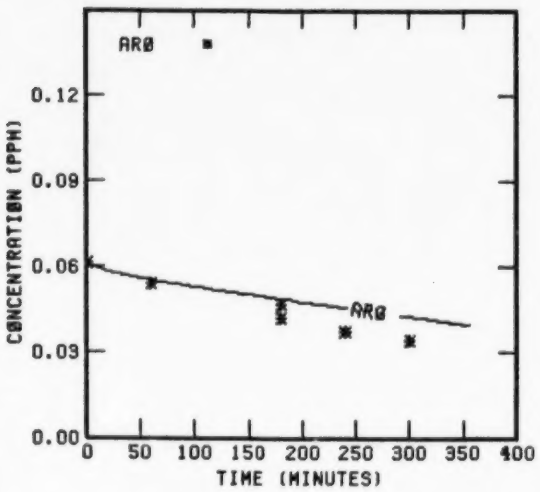
§ Low concentrations include paraffins only; high concentrations include all measured single-bonded carbon.

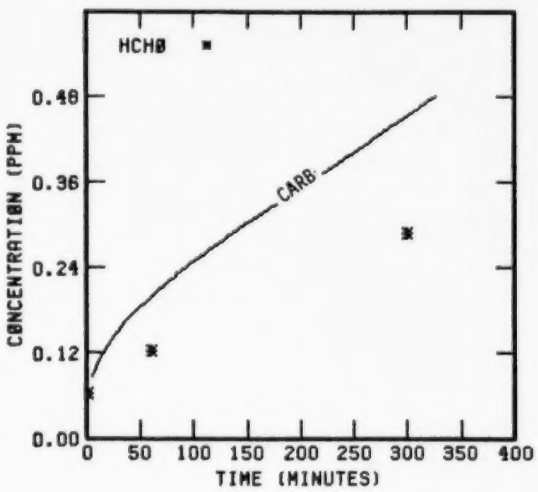
Figure A-1. Simulation results for EC-231.



§ Paraffins only.

Figure A-2. Simulation results for EC-232.





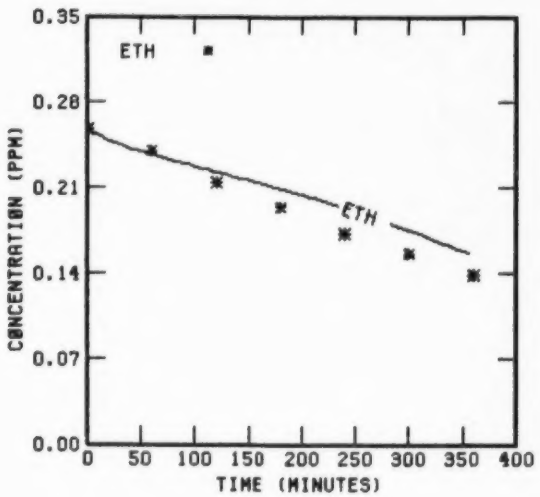
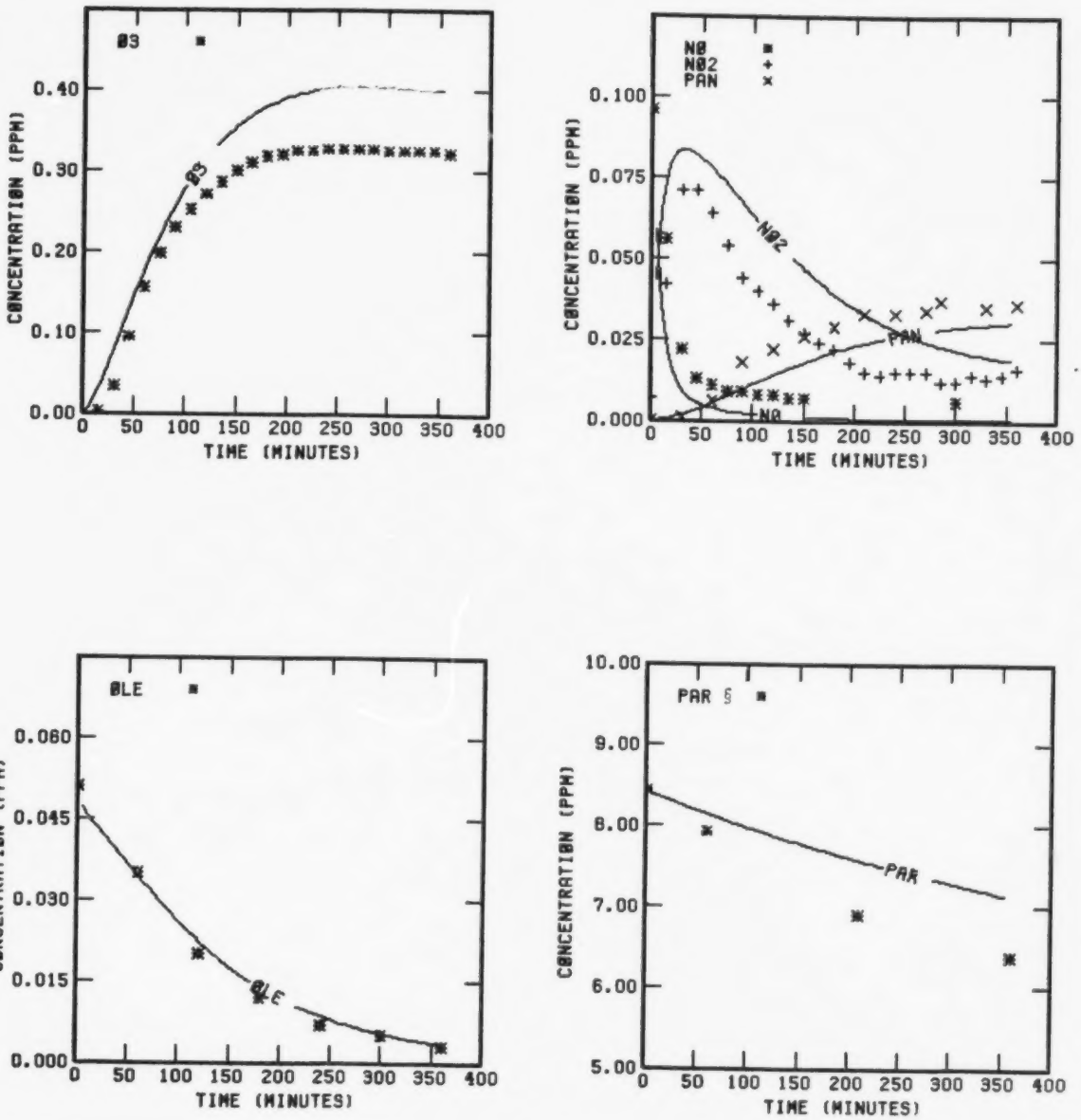
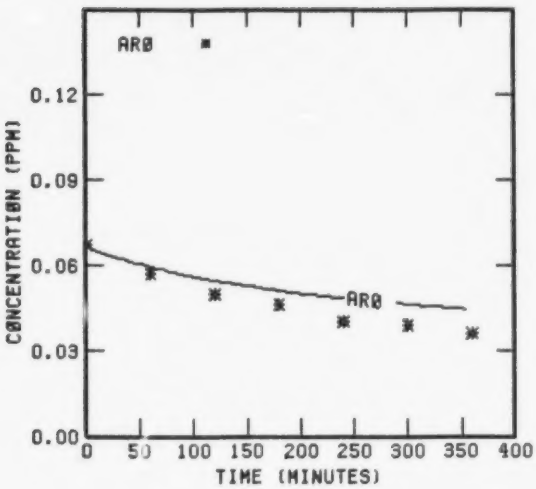


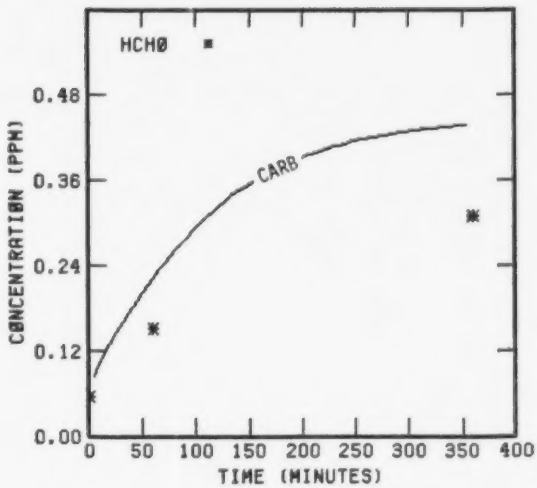
Figure A-2. (concluded)



§ Low concentrations include paraffins only; high concentrations include all measured single-bonded carbon.

Figure A-3. Simulation results for EC-233.





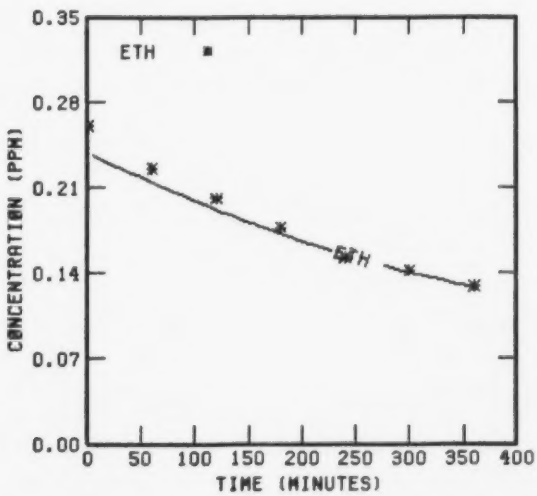
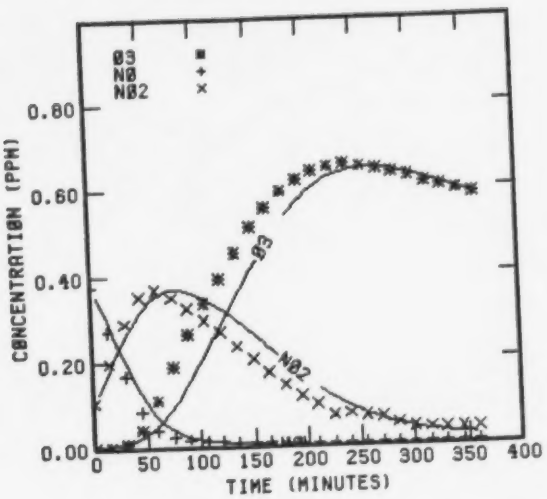
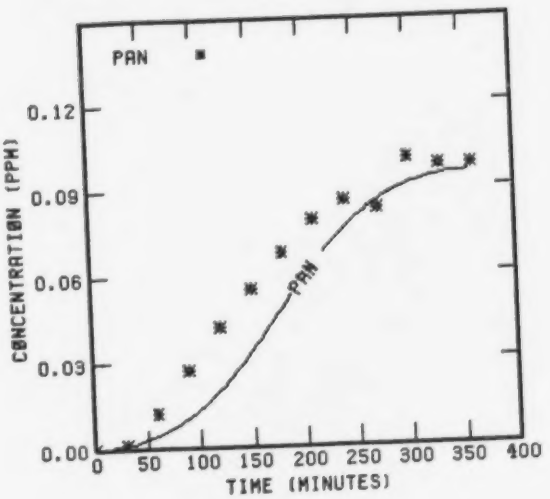
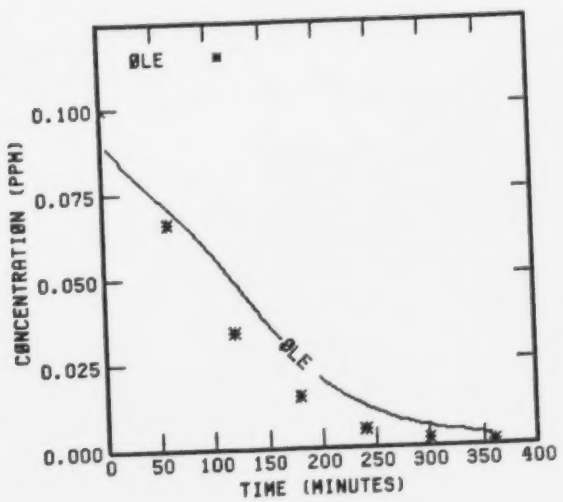
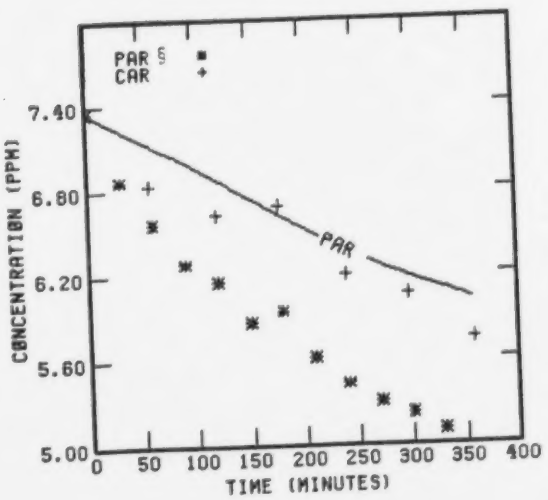


Figure A-3. (concluded)



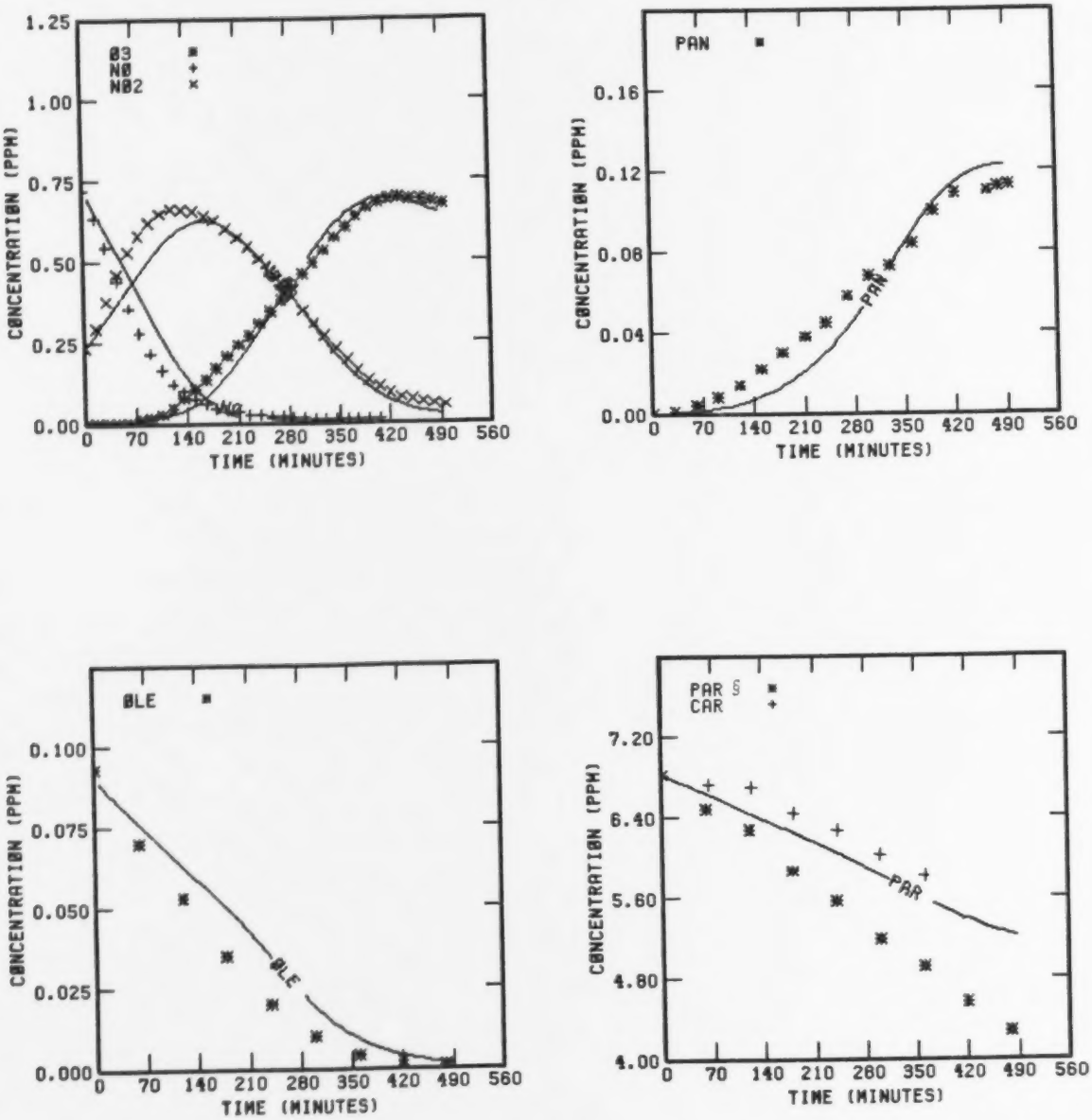






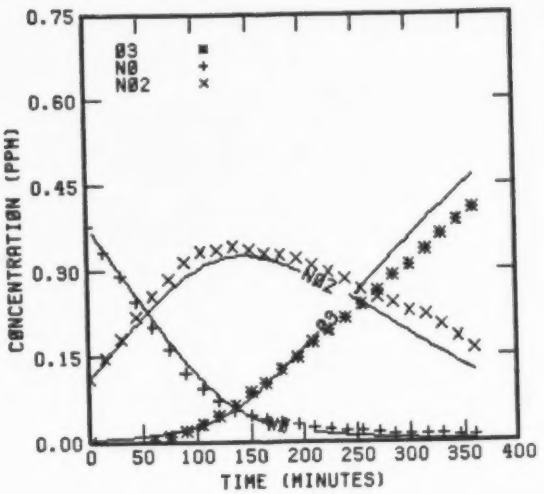
§ Low concentrations include paraffins only; high concentrations include all measured single-bonded carbon.

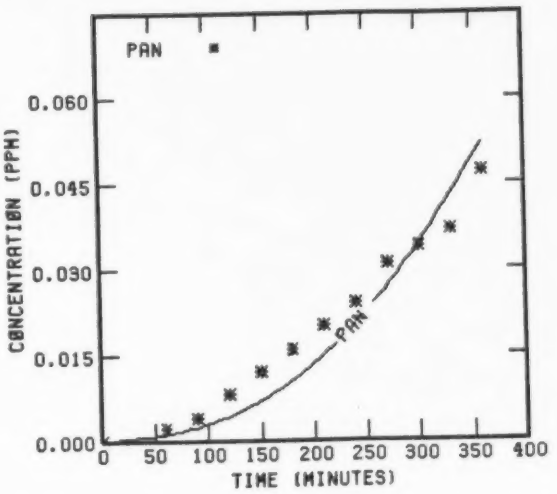
Figure A-4. Simulation results for EC-237.

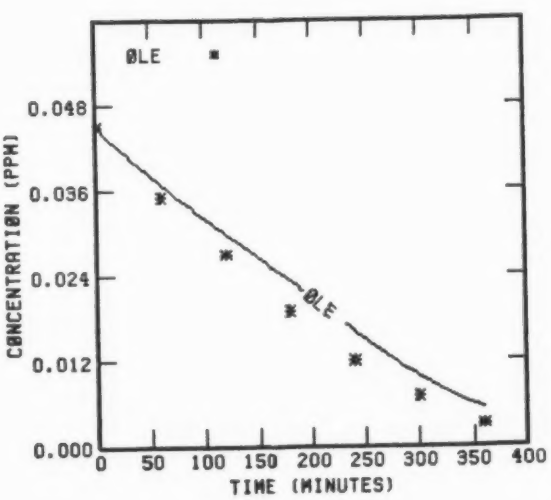


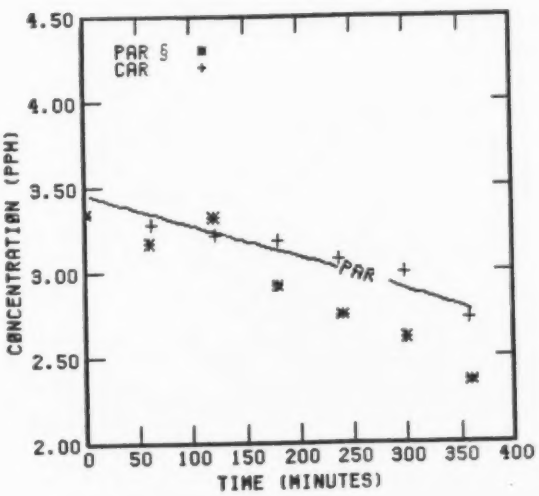
§ Low concentrations include paraffins only; high concentrations include all measured single-bonded carbon.

Figure A-5. Simulation results for EC-238.



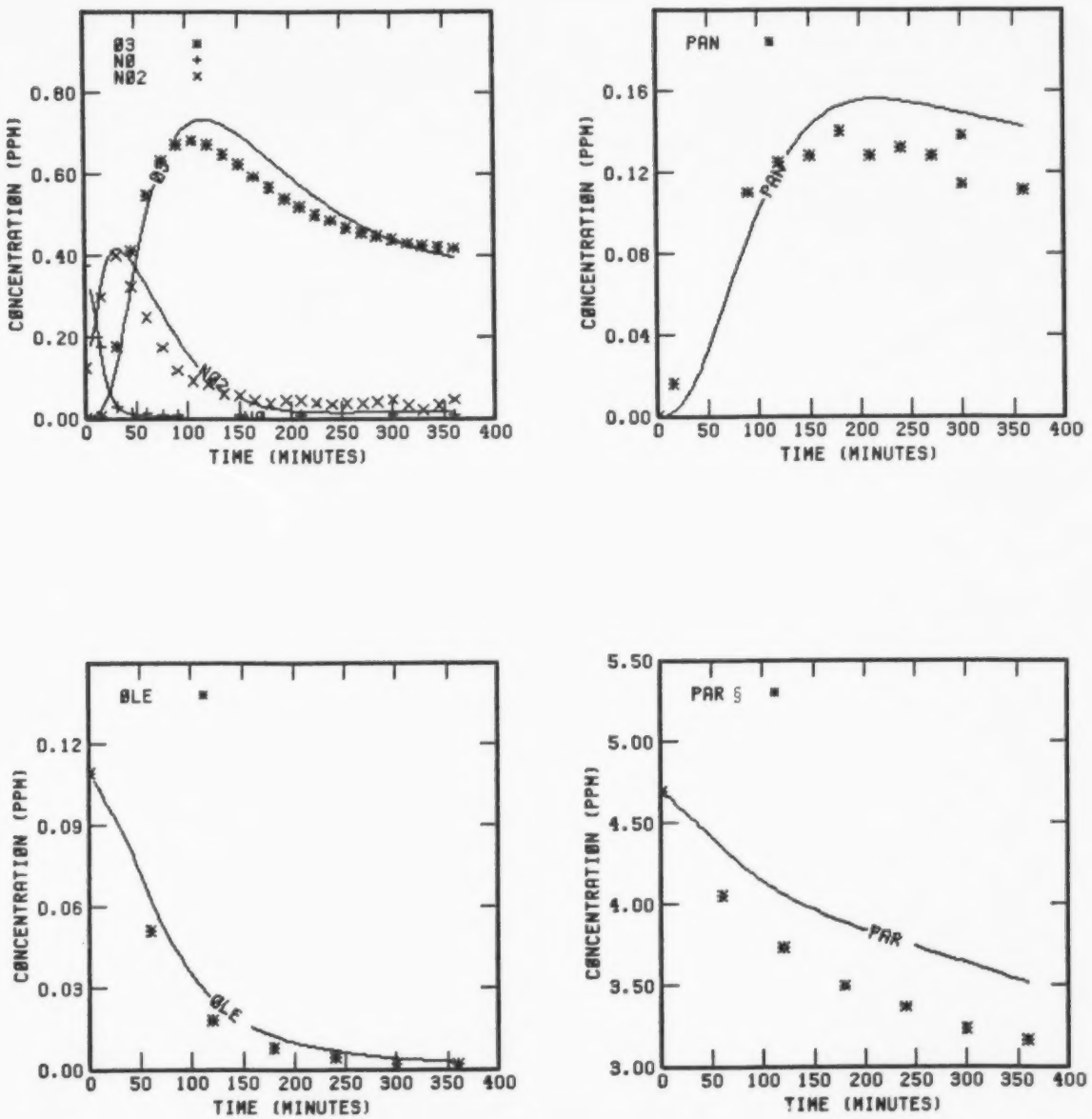






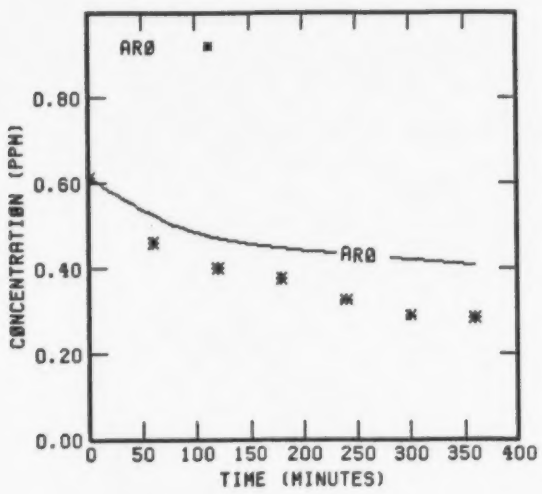
§ Low concentrations include paraffins only; high concentrations include all measured single-bonded carbon.

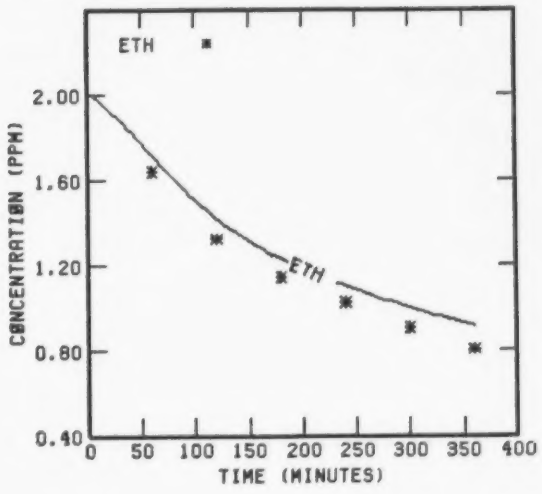
Figure A-6. Simulation results for EC-241.

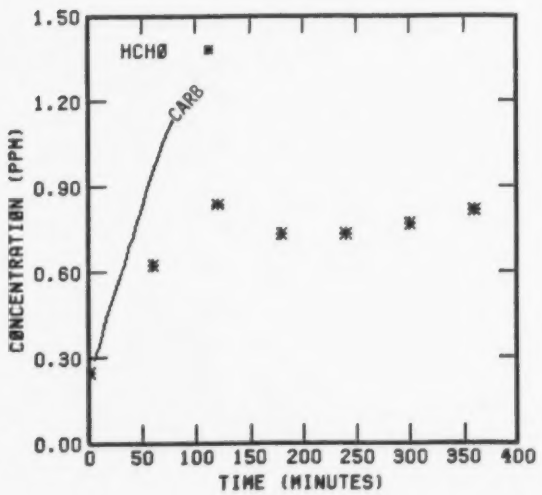


§Paraffins only.

Figure A-7. Simulation results for EC-242.







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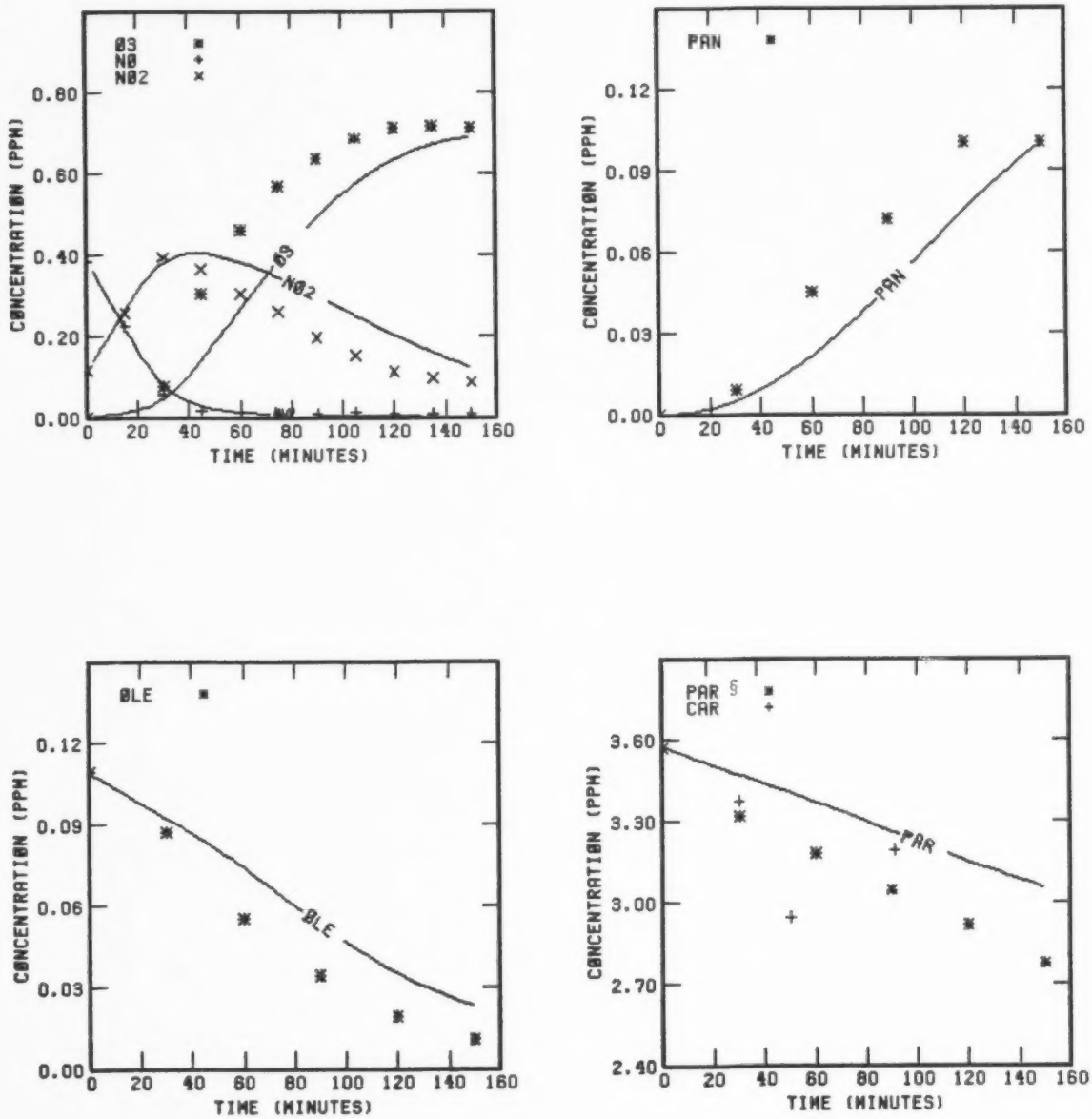
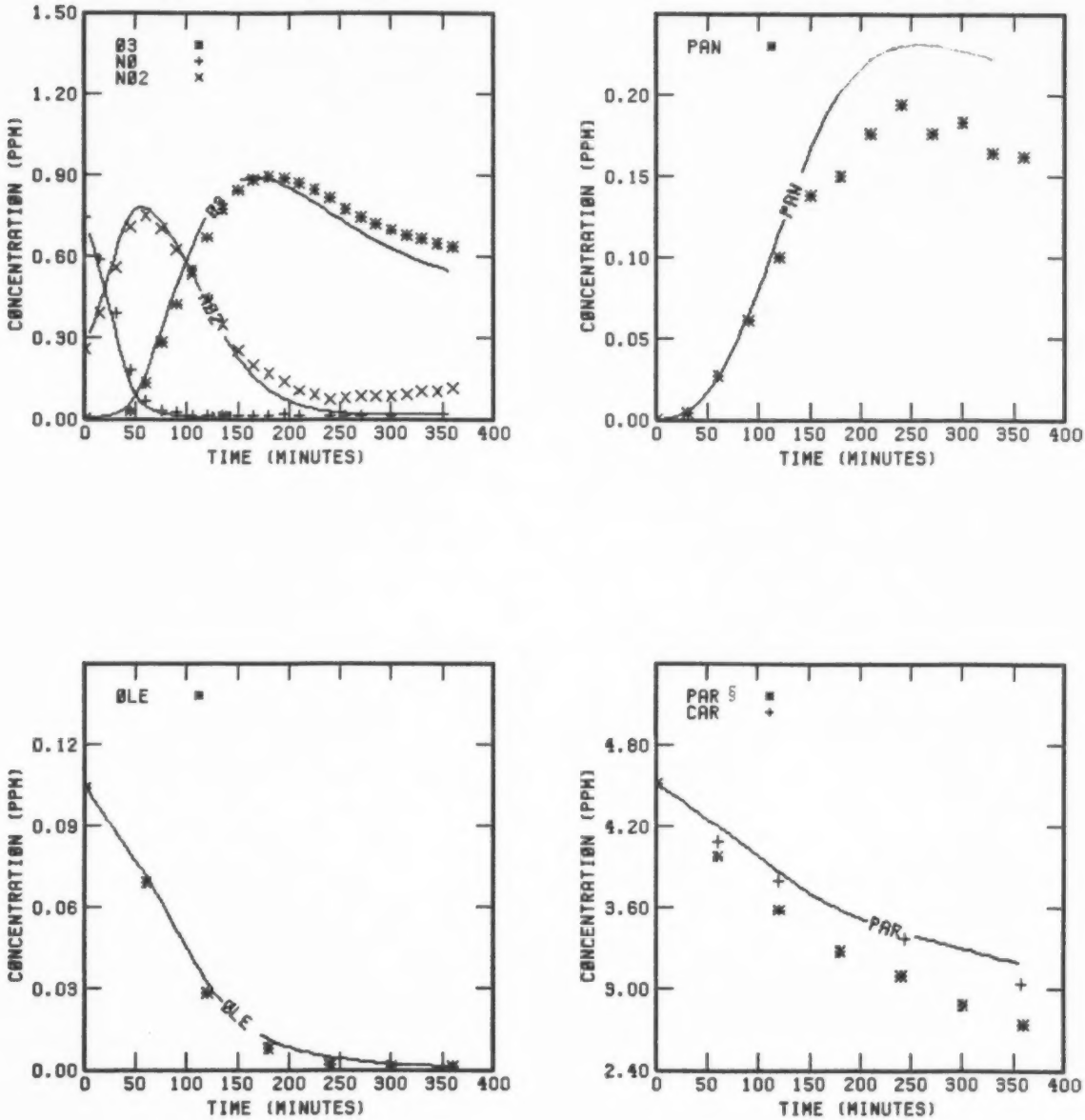


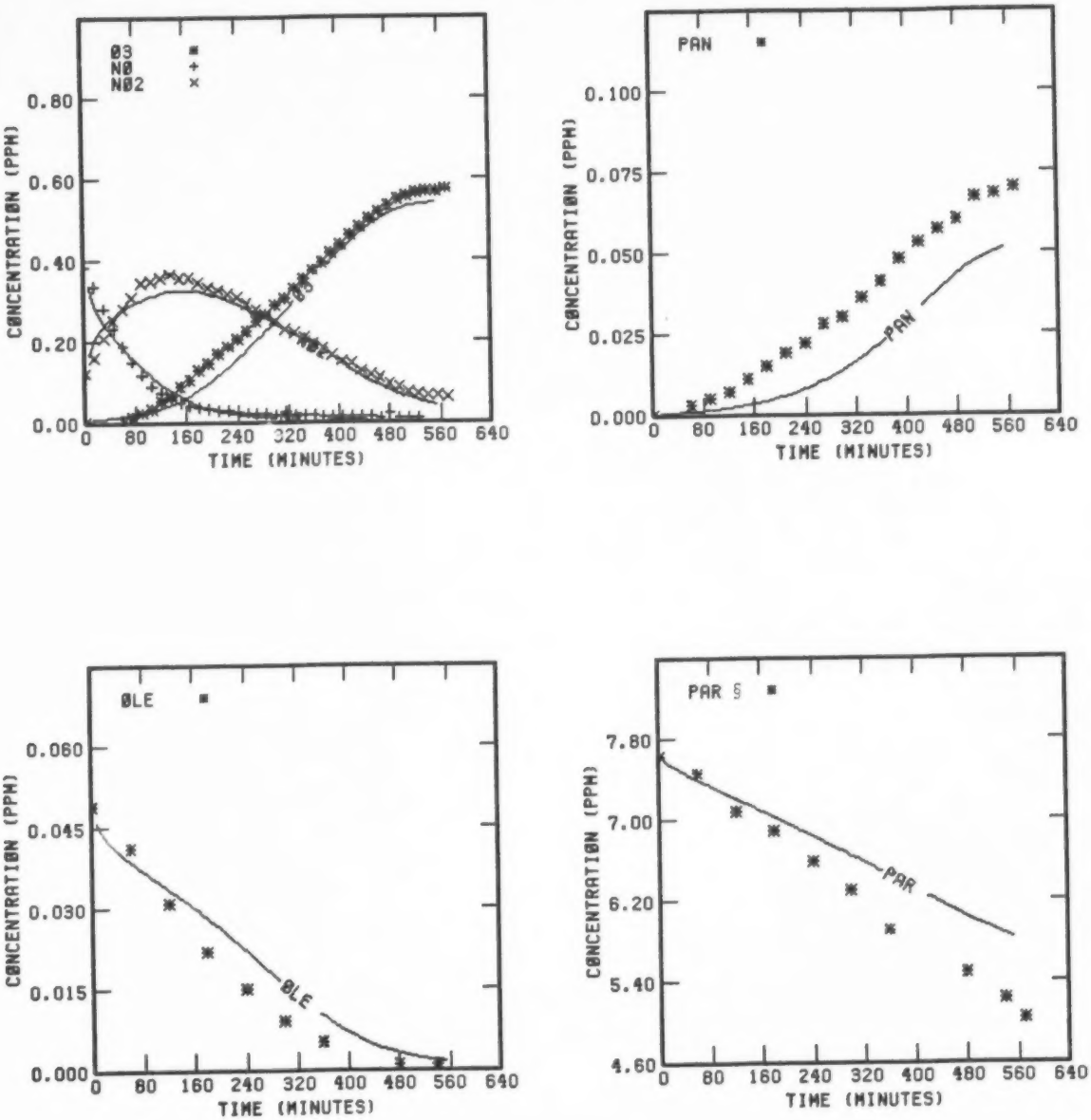
§ Low concentrations include paraffins only; high concentrations include all measured single-bonded carbon.

Figure A-8. Simulation results for EC-243.



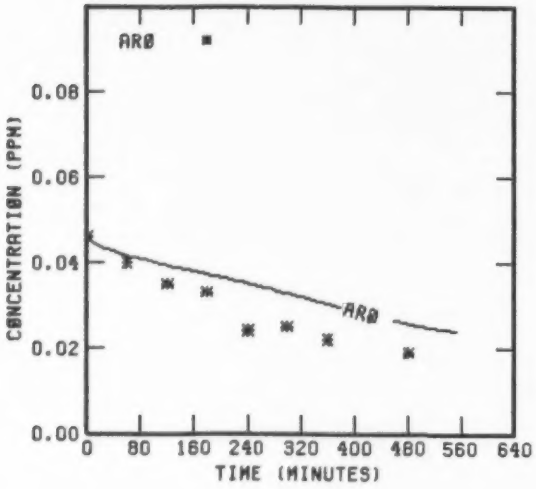
§ Low concentrations include paraffins only; high concentrations include all measured single-bonded carbon.

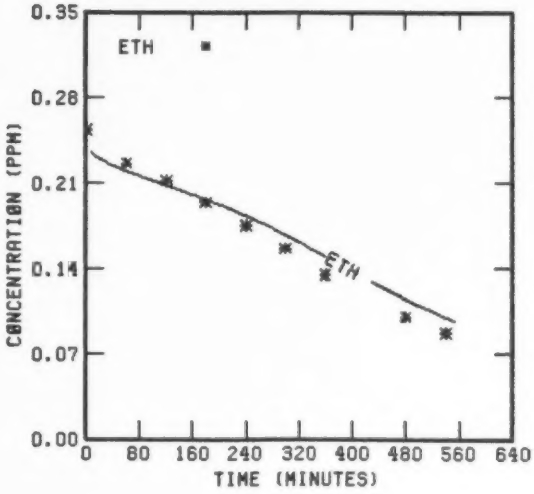
Figure A-9. Simulation results for EC-245.



§ Paraffins only.

Figure A-10. Simulation results for EC-246.





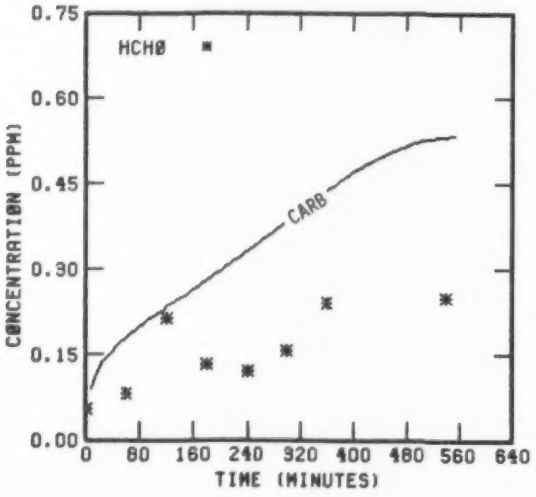
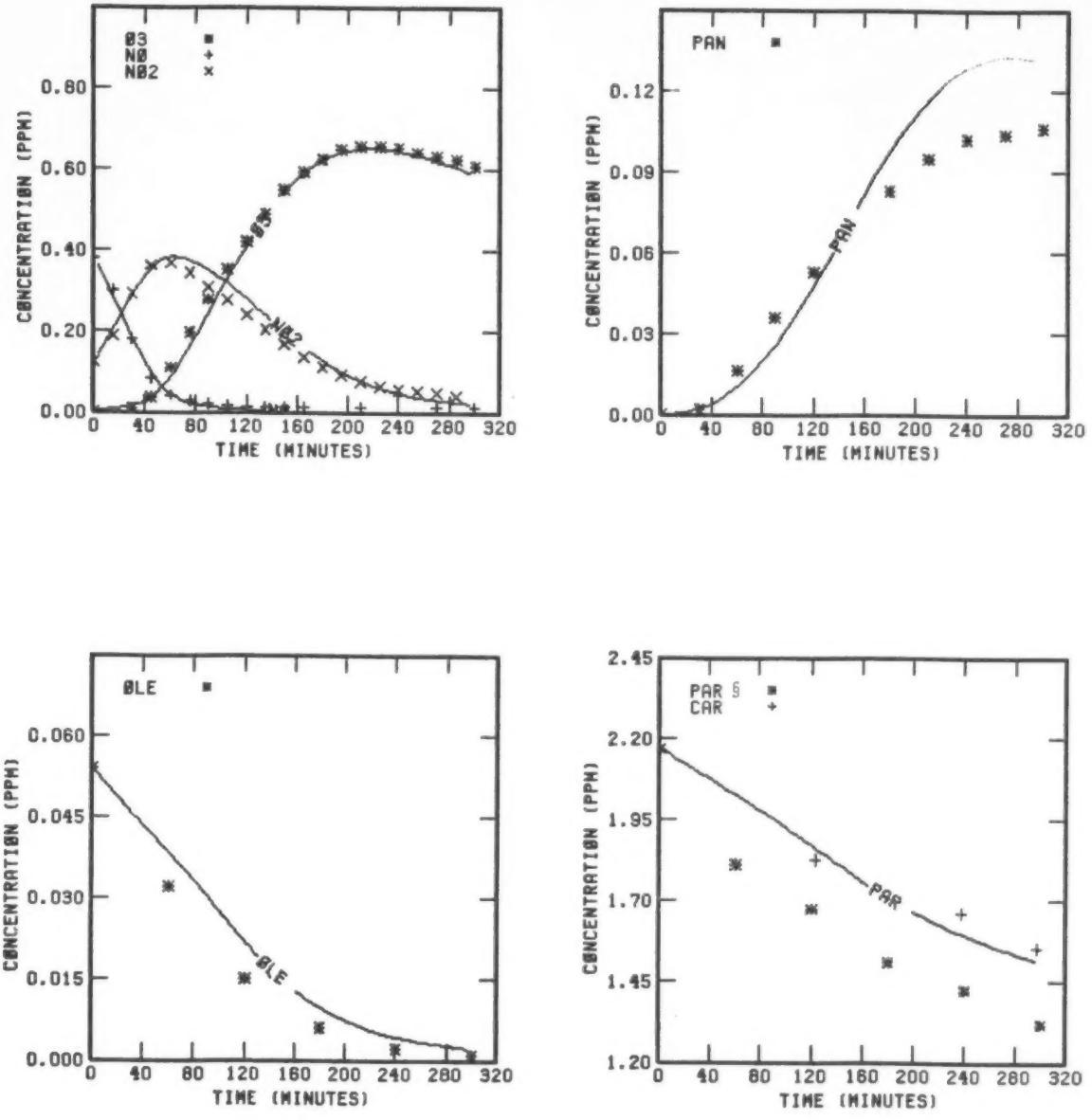


Figure A-10. (concluded)



§ Low concentrations include paraffins only; high concentrations include all measured single-bonded carbon.

Figure A-11. Simulation results for EC-247.

The chamber-dependent reactions used in these simulations are

$$O_3 \text{ and } NO_2 \text{ loss to walls} = 0.0016 \text{ min}^{-1}$$
$$k_{12} = 0.0017 \text{ min}^{-1}$$
$$NO_2 \text{ emission from walls} = 0.1 \text{ ppb min}^{-1} \quad .$$

Photolysis rates are

$$k_1 = 0.3 \text{ min}^{-1}$$
$$k_{37} = 2.7 \times 10^{-4} \text{ min}^{-1}$$
$$k_{38} = 5.4 \times 10^{-4} \text{ min}^{-1}$$
$$k_{67} = 0.0135$$
$$k_{78} = 1 \times 10^{-4} \text{ min}^{-1}.$$

UNIVERSITY OF NORTH CAROLINA OUTDOOR SMOG-CHAMBER EXPERIMENT
(URBAN MIX; TWO-DAY SIMULATION)

The UNC two-day, urban-mix experiment has been previously simulated with CBM-I (Whitten, Hogo, and Killus, 1980). The hydrocarbon mix used contained no aromatics (see table A-2). CBM-III gives results that are comparable to those of CBM-I for mixtures containing olefins and paraffins only (see figure A-12).

Rural North Carolina air is used in the UNC chamber experiments. Background reactivity for the air and chamber is simulated by the following reactions:

NO_2 offgassing from walls: $5 \times 10^{-4} \times k_1$

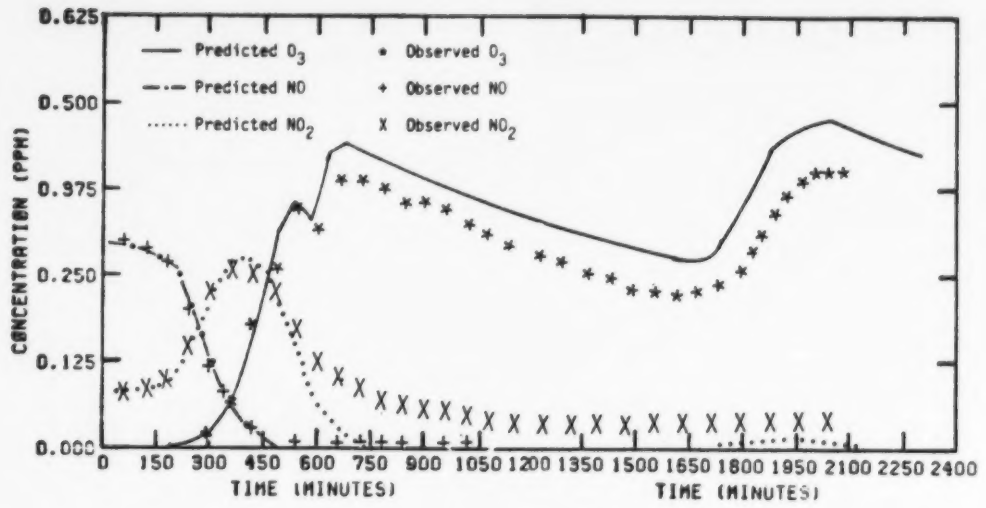
Background reactivity: $OH \rightarrow ME O_2$ $\quad$ $1000 \text{ ppm}^{-1}\text{min}^{-1}$

HO_2 production $\quad 1.5 \times 10^{-4} \; k_1$.

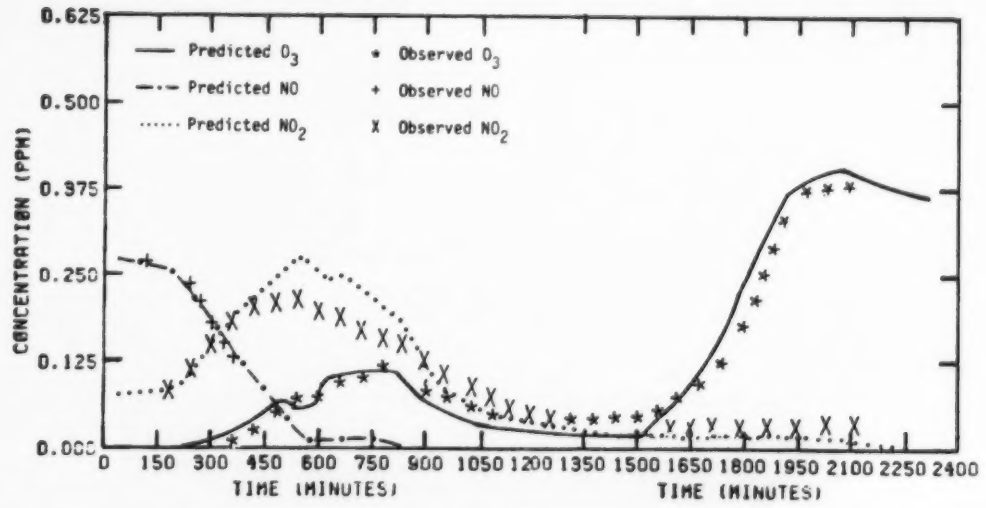
These background reactivity reactions correspond to a hydrocarbon level of about 0.3 ppmC of reactive hydrocarbon and 0.05 ppm formaldehyde. This background reactivity is derived from UNC experiments performed with NO_x added but without added hydrocarbons. Both sides of the chamber were assumed to have an initial condition of 7 ppb HONO.

TABLE A-2. SIMULATED URBAN HYDROCARBON MIXTURE

Class/Compound	Relative Concentration (ppm)	Relative Concentration (ppmC)	Mole Fraction
Acetylenic			
Acetylene	265	530	0.171
Subtotal	265	530	0.171
Paraffins			
Isopentane	172	860	0.111
n-Pentane	286	1430	0.184
2-Methyl pentane	85	510	0.055
2,4-Dimethyl pentane	69	483	0.044
2,2,4-Trimethylene pentane	76	608	0.049
Subtotal	688	3891	0.444
Average carbon number = 5.7			
Olefins			
Butene-1	40	160	0.026
cis-2-Butene	43	172	0.028
2-Methyl-1-butene	26	130	0.017
2-Methyl-2-butene	32	160	0.021
Ethylene	360	720	0.232
Propylene	97	291	0.062
Subtotal	598	1633	0.385
Average carbon number = 2.7			
Total	1551	6,054	1.000

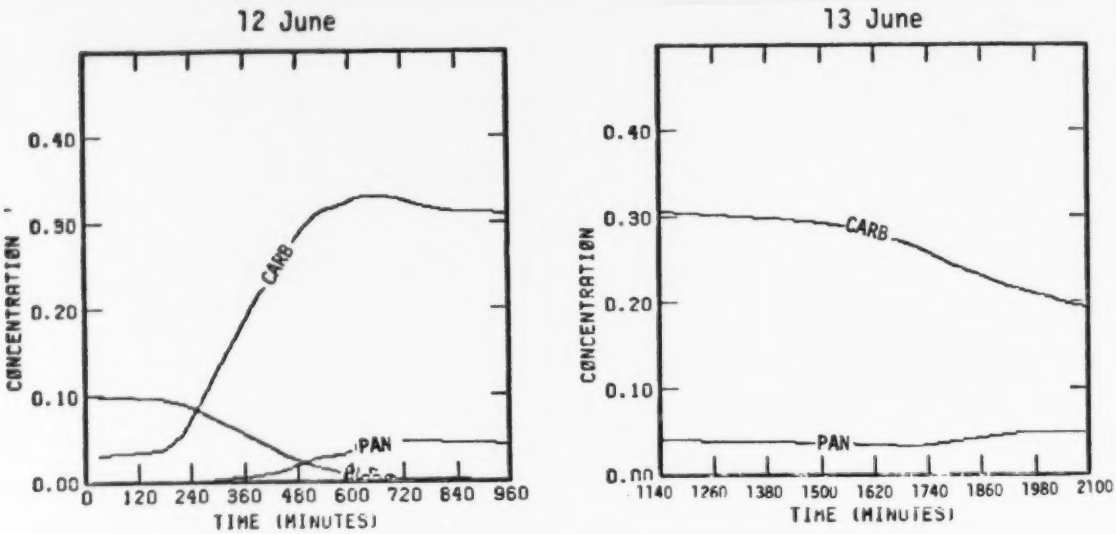


(a) High Hydrocarbon (2.9 ppmC)

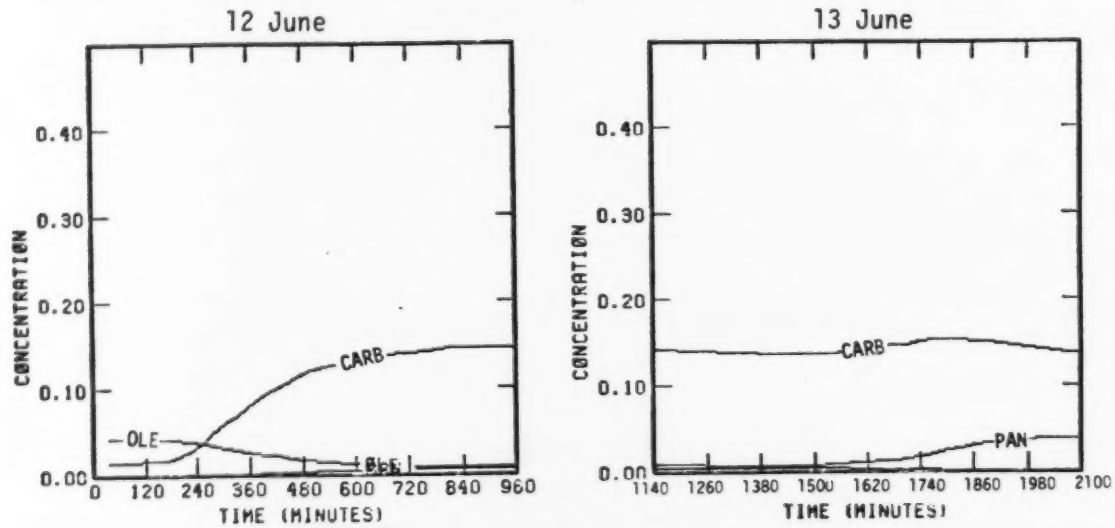


(b) Low Hydrocarbon (1.3 ppmC)

Figure A-12. Results of two-day University of North Carolina smog-chamber run.

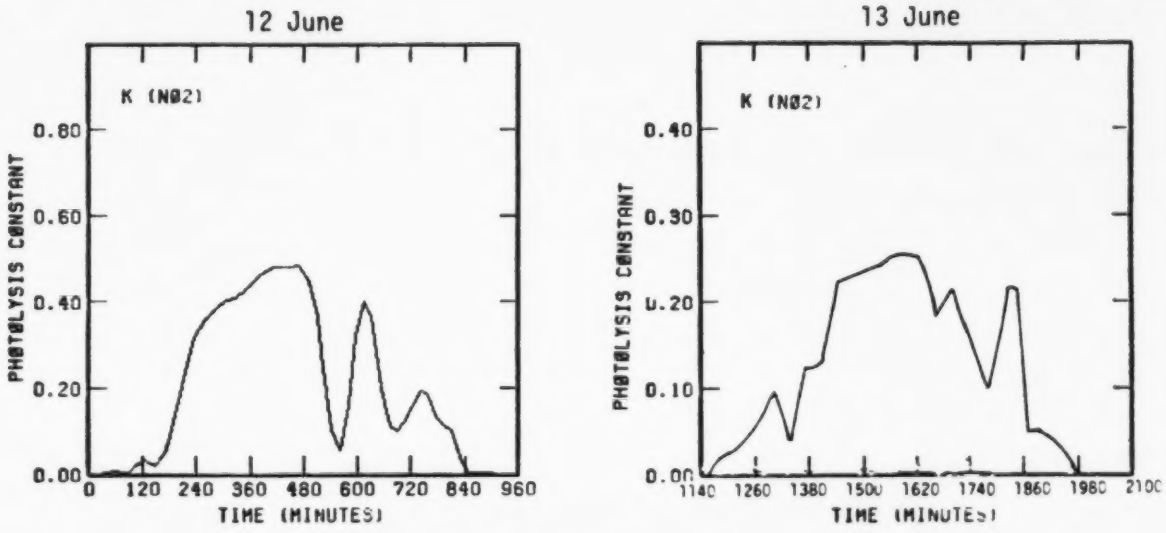


(c) High Hydrocarbon



(d) Low Hydrocarbon

Figure A-12. (continued)



(e) Photolysis Rate

Note: NO_2 data = NO_2 + PAN

Figure A-12. (concluded)

Appendix B

MOLECULAR WEIGHTS AND BOND FRACTIONS OF COMMON MOLECULES

TABLE B-1. MOLECULAR WEIGHTS OF MOLECULES (ORDERED BY SAROAD CODE)

SPECIES NO.	SAROAD CODE	MOLECULAR WEIGHT	CHEMICAL NAME
1	43000	86.00	UNKNOWN SPECIES
2	43105	86.17	ISOMERS OF HEXANE
3	43106	100.20	ISOMERS OF HEPTANE
4	43107	114.23	ISOMERS OF OCTANE
5	43108	128.25	ISOMERS OF NONANE
6	43109	142.28	ISOMERS OF DECANE
7	43110	155.30	ISOMERS OF UNDECANE
8	43111	184.35	ISOMERS OF TRIDECANE
9	43112	170.33	ISOMERS OF DODECANE
10	43113	198.38	ISOMERS OF TETRADECANE
11	43114	212.41	ISOMERS OF PENTADECANE
12	43115	98.19	C-7 CYCLOPARAFFINS
13	43116	112.23	C-8 CYCLOPARAFFINS
14	43117	126.26	C-9 CYCLOPARAFFINS
15	43118	114.23	MINERAL SPIRITS
16	43119	114.23	LACTOL SPIRITS
17	43120	56.10	ISOMERS OF BUTENE
18	43121	70.13	ISOMERS OF PENTENE
19	43122	72.15	ISOMERS OF PENTANE
20	43123	136.24	TERPENES
21	43201	16.04	METHANE
22	43202	30.07	ETHANE
23	43203	28.05	ETHYLENE
24	43204	44.09	PROPANE
25	43205	42.08	PROPYLENE
26	43206	26.04	ACETYLENE
27	43207	42.08	CYCLOPROPANE
28	43208	40.06	PROPYNE
29	43209	40.06	METHYLACETYLENE
30	43211	84.16	3-METHYL-1-PENTENE
31	43212	58.12	N-BUTANE
32	43213	56.10	BUTENE
33	43214	58.12	ISOBUTANE
34	43215	56.10	ISOBUTYLENE
35	43216	56.10	TRANS-2-BUTENE
36	43217	56.10	CIS-2-BUTENE
37	43218	54.09	1,3-BUTADIENE
38	43219	54.09	ETHYLACETYLENE
39	43220	72.15	N-PENTANE
40	43221	72.15	ISOPE NTANE
41	43223	70.14	3-METHYL-1-BUTENE
42	43224	70.13	1-PENTENE

(continued)

TABLE B-1

SPECIES NO.	SAROAD CODE	MOLECULAR WEIGHT	CHEMICAL NAME
43	43225	70.13	2-METHYL-1-BUTENE
44	43226	70.13	TRANS-2-PENTENE
45	43227	70.13	CIS-2-PENTENE
46	43228	70.13	2-METHYL-2-BUTENE
47	43229	86.17	2-METHYL PENTANE
48	43230	86.17	3-METHYL PENTANE
49	43231	86.17	HEXANE
50	43232	100.20	HEPTANE
51	43233	114.23	OCTANE
52	43234	84.16	2,3-DIMETHYL-1-BUTENE
53	43235	128.25	NONANE
54	43236	142.28	N-DECANE
55	43241	156.30	UNDECANE
56	43242	70.14	CYCLOPENTANE
57	43245	84.16	1-HEXENE
58	43248	84.16	CYCLOHEXANE
59	43255	170.33	N-DODECANE
60	43258	184.36	N-TRIDECANE
61	43258	86.17	2,3-DIMETHYLBUTANE
62	43259	198.38	N-TETRADECANE
63	43260	212.41	N-PENTADECANE
64	43260	84.16	2-ETHYL-1-BUTENE
65	43261	98.18	METHYLCYCLOHEXANE
66	43262	84.16	METHYLCYCLOPENTANE
67	43264	98.15	CYCLOHEXANONE
68	43265	40.06	PROPADIENE
69	43268	84.16	C-3-HEXENE
70	43269	84.16	2-METHYL-2-PENTENE
71	43270	84.16	3-METHYL-T-2-PENTENE
72	43271	100.20	2,4-DIMETHYLPENTANE
73	43272	82.14	METHYLCYCLOPENTENE
74	43273	82.14	CYCLOHEXENE
75	43274	100.20	2,3-DIMETHYLPENTANE
76	43275	100.20	2-METHYLHEXANE
77	43276	114.22	2,2,4-TRIMETHYLPENTANE
78	43277	114.22	2,4-DIMETHYLHEXANE
79	43278	114.22	2,5-DIMETHYLHEXANE
80	43279	114.22	2,3,4-TRIMETHYLPENTANE
81	43280	114.22	2,3,3-TRIMETHYLPENTANE
82	43281	226.44	HEXADECANE
83	43282	240.46	HEPTADECANE
84	43283	254.49	OCTADECANE
85	43284	268.51	NONADECANE
86	43285	282.54	EICOSANE
87	43286	296.57	HENEICOSANE
88	43287	310.59	DOCOSANE
89	43288	112.23	ETHYLCYCLOHEXANE
90	43289	84.16	C6 OLEFIN UNK
91	43290	112.23	C8 OLEFIN UNK
92	43291	86.17	2,2-DIMETHYLBUTANE

(continued)

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TABLE B-1

SPECIES NO.	SAROAD CODE	MOLECULAR WEIGHT	CHEMICAL NAME
93	43292	68.11	CYCLOPENTENE
94	43293	84.16	4-METHYL-T-2-PENTENE
95	43294	98.18	C7-OLEFIN UNKNOWN
96	43295	100.20	3-METHYLHEXANE
97	43296	114.23	2.2.3-TRIMETHYLPENTANE
98	43297	114.23	4-METHYLHEPTANE
99	43298	114.23	3-METHYLHEPTANE
100	43299	114.23	2.2.5-TRIMETHYLPENTANE
101	43301	32.04	METHYL ALCOHOL
102	43302	46.07	ETHYL ALCOHOL
103	43303	60.09	N-PROPYL ALCOHOL
104	43304	60.09	ISOPROPYL ALCOHOL
105	43305	74.12	N-BUTYL ALCOHOL
106	43306	74.12	ISOBUTYL ALCOHOL
107	43307	118.17	BUTYL CELLOSOLVE
108	43309	74.12	TERT-BUTYL ALCOHOL
109	43310	76.11	METHYL CELLOSOLVE
110	43311	90.12	CELLOSOLVE
111	43312	112.23	1-T-2-C-4-TM-CYCLOPENTANE
112	43320	116.16	DIACETONE ALCOHOL
113	43351	74.12	ETHYL ETHER
114	43367	106.12	GLYCOL ETHER
115	43368	62.07	GLYCOL
116	43369	76.00	PROPYLENE GLYCOL
117	43370	62.07	ETHYLENE GLYCOL
118	43392	72.10	TETRAHYDROFURAN
119	43404	60.05	ACETIC ACID
120	43432	74.08	METHYL ACETATE
121	43433	88.10	ETHYL ACETATE
122	43434	102.13	PROPYL ACETATE
123	43435	116.16	N-BUTYL ACETATE
124	43438	100.11	ETHYL ACRYLATE
125	43443	132.00	CELLOSOLVE ACETATE
126	43444	104.00	ISOPROPYL ACETATE
127	43445	140.00	METHYL AMYL ACETATE
128	43446	116.16	ISOBUTYL ACETATE
129	43450	73.09	DIMETHYLFORMAMIDE
130	43451	144.21	ISOBUTYL ISOBUTYRATE
131	43452	132.00	2-ETHOXYETHYL ACETATE
132	43502	30.03	FORMALDEHYDE
133	43503	44.05	ACETALDEHYDE
134	43504	58.08	PROPRIONALDEHYDE
135	43510	72.12	BUTYRALDEHYDE
136	43511	58.08	C3 ALDEHYDE
137	43512	86.14	C5 ALDEHYDE
138	43513	128.21	C8 ALDEHYDE
139	43551	58.08	ACETONE
140	43552	72.10	METHYL ETHYL KETONE
141	43559	100.16	METHYL N-BUTYL KETONE
142	43560	100.16	METHYL ISOBUTYL KETONE

(continued)

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TABLE B-1

SPECIES NO.	SAROAD CODE	MOLECULAR WEIGHT	CHEMICAL NAME
143	43601	44.05	ETHYLENE OXIDE
144	43602	58.08	PROPYLENE OXIDE
145	43702	41.05	ACETONITRILE
146	43704	53.06	ACRYLONITRILE
147	43721	45.09	ETHYLAMINE
148	43740	59.11	TRIMETHYL AMINE
149	43801	50.49	METHYL CHLORIDE
150	43801	112.56	CHLOROBENZENE
151	43802	84.94	DICHLOROMETHANE
152	43803	119.39	CHLOROFORM
153	43804	153.84	CARBON TETRACHLORIDE
154	43807	331.67	CARBON TETRABROMIDE
155	43811	137.37	TRICHLOROFLUOROMETHANE
156	43812	64.52	ETHYL CHLORIDE
157	43813	98.97	1.1-DICHLOROETHANE
158	43814	133.42	1.1.1-TRICHLOROETHANE
159	43815	99.00	ETHYLENE DICHLORIDE
160	43817	165.85	PERCHLOROETHYLENE
161	43819	173.85	METHYLENE BROMIDE
162	43820	131.66	1.1.2-TRICHLOROETHANE
163	43821	187.38	TRICHLOROTRIFLUOROETHANE
164	43822	92.00	TRIMETHYLFLUOROSILANE
165	43823	120.92	DICHLORODIFLUOROMETHANE
166	43824	131.40	TRICHLOROETHYLENE
167	43860	62.50	VINYL CHLORIDE
168	45101	114.23	NAPTHA
169	45102	106.16	ISOMERS OF XYLENE
170	45103	134.21	DIMETHYLETHYLBENZENE
171	45104	120.19	ISOMERS OF ETHYLTOLUENE
172	45105	134.21	ISOMERS OF BUTYLBENZENE
173	45106	134.21	ISOMERS OF DIETHYLBENZENE
174	45107	120.19	ISOMERS OF TRIMETHYLBENZENE
175	45108	120.19	ISOMERS OF PROPYLBENZENE
176	45201	78.11	BENZENE
177	45202	92.13	TOLUENE
178	45203	106.16	ETHYLBENZENE
179	45204	106.16	O-XYLENE
180	45205	106.16	M-XYLENE
181	45206	106.16	P-XYLENE
182	45207	120.19	1.3.5-TRIMETHYLBENZENE
183	45208	120.19	1.2.4-TRIMETHYLBENZENE
184	45209	120.19	N-PROPYLBENZENE
185	45211	120.19	O-ETHYLTOLUENE
186	45212	120.19	M-ETHYLTOLUENE
187	45215	134.21	TERT-BUTYLBENZENE
188	45216	134.21	SEC-BUTYLBENZENE
189	45220	104.14	STYRENE
190	45221	118.15	A-METHYLSTYRENE
191	45225	120.19	1.2.3-TRIMETHYLBENZENE
192	45232	134.21	TETRAMETHYLBENZENE
193	45233	148.23	TRI/TETRAALKYL BENZENE
194	45234	134.21	ISOMERS OF METHYLPROP. BENZENE
195	45300	94.11	PHENOLS
196	45401	230.00	XYLENE BASE ACIDS
197	46201	88.12	1.4-DIOXANE

(concluded)

TABLE B-2. BOND GROUPS PER MOLECULE (ORDERED BY SAROAD CODE)

SPECIES NO.	CHEMICAL NAME	SPECIES PROFILES BY BOND GROUP					
		OLE	PAR	ARO	CARB	ETH	UNREACTIVE
1	UNKNOWN SPECIES	0.10	4.00	0.25	0.32	0.16	
2	ISOMERS OF HEXANE		6.00				
3	ISOMERS OF HEPTANE		7.00				
4	ISOMERS OF OCTANE		8.00				
5	ISOMERS OF NONANE		9.00				
6	ISOMERS OF DECANE		10.00				
7	ISOMERS OF UNDECANE		11.00				
8	ISOMERS OF TRIDECANE		13.00				
9	ISOMERS OF DODECANE		12.00				
10	ISOMERS OF TETRADECANE		14.00				
11	ISOMERS OF PENTADECANE		15.00				
12	C-7 CYCLOPARAFFINS		6.00		1.00		
13	C-8 CYCLOPARAFFINS		7.00		1.00		
14	C-9 CYCLOPARAFFINS		8.00		1.00		
15	MINERAL SPIRITS		7.00		1.00		
16	LACTOL SPIRITS		8.00				
17	ISOMERS OF BUTENE		2.00		2.00		
18	ISOMERS OF PENTENE		3.00		2.00		
19	ISOMERS OF PENTANE		5.00				
20	TERPENES	1.00	8.00				
21	METHANE						1.00
22	ETHANE						2.00
23	ETHYLENE					1.00	
24	PROPANE		1.50				1.50
25	PROPYLENE	1.00	1.00				
26	ACETYLENE						1.00
27	CYCLOPROPANE		2.00		1.00		
28	PROPYNE		2.00				1.00
29	METHYLACETYLENE		1.50				1.50
30	3-METHYL-1-PENTENE		6.00				
31	N-BUTANE		4.00				
32	BUTENE	1.00	2.00				
33	ISOBUTANE		4.00				
34	ISOBUTYLENE	1.00	2.00				
35	TRANS-2-BUTENE		2.00		2.00		
36	CIS-2-BUTENE		2.00		2.00		
37	1,3-BUTADIENE	1.00			2.00		
38	ETHYLACETYLENE		4.00				
39	N-PENTANE		5.00				
40	ISOPENTANE		5.00				

(continued)

TABLE B-2

SPECIES PROFILES BY BOND GROUP

SPECIES NO.	CHEMICAL NAME	OLE	PAR	ARO	CARB	ETH	UNREACTIVE
41	3-METHYL-1-BUTENE	1.00	3.00				
42	1-PENTENE	1.00	3.00				
43	2-METHYL-1-BUTENE	1.00	3.00				
44	TRANS-2-PENTENE		3.00		2.00		
45	CIS-2-PENTENE		3.00		2.00		
46	2-METHYL-2-BUTENE		3.00		2.00		
47	2-METHYL PENTANE		6.00				
48	3-METHYL PENTANE		6.00				
49	HEXANE		6.00				
50	HEPTANE		7.00				
51	OCTANE		8.00				
52	2,3-DIMETHYL-1-BUTENE	1.00	4.00				
53	NONANE		9.00				
54	N-DECANE		10.00				
55	UNDECANE		11.00				
56	CYCLOPENTANE		4.00		1.00		
57	1-HEXENE	1.00	4.00				
58	CYCLOHEXANE		5.00		1.00		
59	N-DODECANE		12.00				
60	N-TRIDECANE		13.00				
61	2,3-DIMETHYLBUTANE		6.00				
62	N-TETRADECANE		14.00				
63	N-PENTADECANE		15.00				
64	2-ETHYL-1-BUTENE	1.00	4.00				
65	METHYLCYCLOHEXANE		6.00		1.00		
66	METHYLCYCLOPENTANE		5.00		1.00		
67	CYCLOHEXANONE		4.00		2.00		
68	PROPADIENE		1.00		2.00		
69	C-3-HEXENE	1.00	4.00				
70	2-METHYL-2-PENTENE		4.00		2.00		
71	3-METHYL-T-2-PENTENE		4.00		2.00		
72	2,4-DIMETHYLPENTANE		7.00				
73	METHYLCYCLOPENTENE	1.00	4.00				
74	CYCLOHEXENE	1.00	4.00				
75	2,3-DIMETHYLPENTANE		7.00				
76	2-METHYLHEXANE		7.00				
77	2,2,4-TRIMETHYLPENTANE		8.00				
78	2,4-DIMETHYLHEXANE		8.00				
79	2,5-DIMETHYLHEXANE		8.00				
80	2,3,4-TRIMETHYLPENTANE		8.00				

(continued)

TABLE B-2

SPECIES PROFILES BY BOND GROUP

SPECIES NO.	CHEMICAL NAME	OLE	PAR	ARO	CARB	ETH	UNREACTIVE
81	2,3,3-TRIMETHYLPENTANE		6.00				
82	HEXADECANE		16.00				
83	HEPTADECANE		17.00				
84	OCTADECANE		18.00				
85	NONADECANE		19.00				
86	EICOSANE		20.00				
87	HENEICOSANE		21.00				
88	DOCOSANE		22.00				
89	ETHYLCYCLOHEXANE		7.00		1.00		
90	C6 OLEFIN UNK	1.00	4.00				
91	C8 OLEFIN UNK	1.00	6.00				
92	2,2-DIMETHYLBUTANE		6.00				
93	CYCLOPENTENE	1.00	3.00				
94	4-METHYL-T-2-PENTENE		4.00		2.00		
95	C7-OLEFIN UNKNOWN	1.00	5.00				
96	3-METHYLHEXANE		7.00				
97	2,2,3-TRIMETHYLPENTANE		8.00				
98	4-METHYLHEPTANE		8.00				
99	3-METHYLHEPTANE		8.00				
100	2,2,5-TRIMETHYLPENTANE		8.00				
101	METHYL ALCOHOL		1.00				
102	ETHYL ALCOHOL		2.00				
103	N-PROPYL ALCOHOL		3.00				
104	ISOPROPYL ALCOHOL		3.00				
105	N-BUTYL ALCOHOL		4.00				
106	ISOBUTYL ALCOHOL		4.00				
107	BUTYL CELLOSOLVE		5.00		1.00		
108	TERT-BUTYL ALCOHOL		3.00		1.00		
109	METHYL CELLOSOLVE		2.00		1.00		
110	CELLOSOLVE		3.00		1.00		
111	1-T-2-C-4-TM-CYCLOPENTANE		7.00		1.00		
112	DIACETONE ALCOHOL		5.00		1.00		
113	ETHYL ETHER		3.00		1.00		
114	GLYCOL ETHER		1.00		1.00		
115	GLYCOL		1.00		1.00		
116	PROPYLENE GLYCOL		2.00		1.00		
117	ETHYLENE GLYCOL		1.00		1.00		
118	TETRAHYDROFURAN		3.00		1.00		
119	ACETIC ACID		2.00				
120	METHYL ACETATE						3.00

(continued)

TABLE B-2

SPECIES PROFILES BY BOND GROUP

SPECIES NO.	CHEMICAL NAME	OLE	PAR	ARO	CARB	ETH	UNREACTIVE
121	ETHYL ACETATE		3.00		1.00		
122	PROPYL ACETATE		4.00		1.00		
123	N-BUTYL ACETATE		5.00		1.00		
124	ETHYL ACRYLATE		3.00		2.00		
125	CELLOSOLVE ACETATE		4.00		2.00		
126	ISOPROPYL ACETATE		5.00				
127	METHYL AMYL ACETATE		8.00				
128	ISOBUTYL ACETATE		6.00				
129	DIMETHYLFORMAMIDE						3.00
130	ISOBUTYL ISOBUTYRATE		7.00		1.00		
131	2-ETHOXYETHYL ACETATE		4.00		2.00		
132	FORMALDEHYDE				1.00		
133	ACETALDEHYDE		1.00		1.00		
134	PROPRIONALDEHYDE		2.00		1.00		
135	BUTYRALDEHYDE		3.00		1.00		
136	C3 ALDEHYDE		2.00		1.00		
137	C5 ALDEHYDE		4.00		1.00		
138	C8 ALDEHYDE		7.00		1.00		
139	ACETONE		2.00		1.00		
140	METHYL ETHYL KETONE		3.00		1.00		
141	METHYL N-BUTYL KETONE		5.00		1.00		
142	METHYL ISOBUTYL KETONE		5.00		1.00		
143	ETHYLENE OXIDE		1.00				1.00
144	PROPYLENE OXIDE		2.00				1.00
145	ACETONITRILE		1.00				1.00
146	ACRYLONITRILE	1.00	1.00				
147	ETHYLAMINE		1.00				1.00
148	TRIMETHYL AMINE		3.00				
149	METHYL CHLORIDE						1.00
150	CHLOROBENZENE						6.00
151	DICHLOROMETHANE						1.00
152	CHLOROFORM						1.00
153	CARBON TETRACHLORIDE						1.00
154	CARBON TETRABROMIDE						1.00
155	TRICHLOROFLUOROMETHANE						1.00
156	ETHYL CHLORIDE						2.00
157	1,1-DICHLOROETHANE						2.00
158	1,1,1-TRICHLOROETHANE						2.00
159	ETHYLENE DICHLORIDE					1.00	
160	PERCHLOROETHYLENE						2.00

(continued)

TABLE B-2

SPECIES PROFILES BY BOND GROUP

SPECIES NO.	CHEMICAL NAME	OLE	PAR	ARO	CARB	ETH	UNREACTIVE
161	METHYLENE BROMIDE						1.00
162	1,1,2-TRICHLOROETHANE						2.00
163	TRICHLOROTRIFLUOROETHANE						2.00
164	TRIMETHYLFLUOROSILANE						3.00
165	DICHLORODIFLUOROMETHANE						1.00
166	TRICHLOROETHYLENE					1.00	
167	VINYL CHLORIDE					1.00	
168	NAPTHA		8.00				
169	ISOMERS OF XYLENE		2.00	1.00			
170	DIMETHYLETHYLBENZENE		4.00	1.00			
171	ISOMERS OF ETHYLTOLUENE		3.00	1.00			
172	ISOMERS OF BUTYLBENZENE		4.00	1.00			
173	ISOMERS OF DIETHYLBENZENE		4.00	1.00			
174	ISOMERS OF TRIMETHYLBENZENE		3.00	1.00			
175	ISOMERS OF PROPYLBENZENE		3.00	1.00			
176	BENZENE						6.00
177	TOLUENE		1.00	1.00			
178	ETHYLBENZENE		2.00	1.00			
179	O-XYLENE		2.00	1.00			
180	M-XYLENE		2.00	1.00			
181	P-XYLENE		2.00	1.00			
182	1,3,5-TRIMETHYLBENZENE		3.00	1.00			
183	1,2,4-TRIMETHYLBENZENE		3.00	1.00			
184	N-PROPYLBENZENE		3.00	1.00			
185	O-ETHYLTOLUENE		3.00	1.00			
186	M-ETHYLTOLUENE		3.00	1.00			
187	TERT-BUTYLBENZENE		4.00	1.00			
188	SEC-BUTYLBENZENE		4.00	1.00			
189	STYRENE		1.00	1.00	1.00		
190	A-METHYLSTYRENE		2.00	1.00	1.00		
191	1,2,3-TRIMETHYLBENZENE		3.00	1.00			
192	TETRAMETHYLBENZENE		4.00	1.00			
193	TRI/TETRAALKYL BENZENE		5.00	1.00			
194	ISOMERS OF METHYLPROP. BENZENE		4.00	1.00			
195	PHENOLS						6.00
196	XYLENE BASE ACIDS		2.00	1.00			
197	1,4-DIOXANE	1.00	2.00		2.00		

(concluded)

TABLE B-3. MOLECULAR WEIGHT OF MOLECULES
(IN ALPHABETICAL ORDER)

SPECIES NO.	SAROAD CODE	MOLECULAR WEIGHT	CHEMICAL NAME
1	43814	133.42	1,1,1-TRICHLORDETHANE
2	43820	131.66	1,1,2-TRICHLORDETHANE
3	43813	98.97	1,1-DICHLORDETHANE
4	45225	120.19	1,2,3-TRIMETHYLBENZENE
5	45208	120.19	1,2,4-TRIMETHYLBENZENE
6	45207	120.19	1,3,5-TRIMETHYLBENZENE
7	43218	54.09	1,3-BUTADIENE
8	46201	88.12	1,4-DIOXANE
9	43245	84.16	1-HEXENE
10	43224	70.13	1-PENTENE
11	43312	112.23	1-T-2-C-4-TM-CYCLOPENTANE
12	43296	114.23	2,2,3-TRIMETHYLPENTANE
13	43276	114.22	2,2,4-TRIMETHYLPENTANE
14	43299	114.23	2,2,5-TRIMETHYLPENTANE
15	43291	86.17	2,2-DIMETHYLBUTANE
16	43280	114.22	2,3,3-TRIMETHYLPENTANE
17	43279	114.22	2,3,4-TRIMETHYLPENTANE
18	43234	84.16	2,3-DIMETHYL-1-BUTENE
19	43258	86.17	2,3-DIMETHYLBUTANE
20	43274	100.20	2,3-DIMETHYLPENTANE
21	43277	114.22	2,4-DIMETHYLHEXANE
22	43271	100.20	2,4-DIMETHYLPENTANE
23	43278	114.22	2,5-DIMETHYLHEXANE
24	43452	132.00	2-ETHOXYETHYL ACETATE
25	43260	84.16	2-ETHYL-1-BUTENE
26	43229	86.17	2-METHYL PENTANE
27	43225	70.13	2-METHYL-1-BUTENE
28	43228	70.13	2-METHYL-2-BUTENE
29	43269	84.16	2-METHYL-2-PENTENE
30	43275	100.20	2-METHYLHEXANE
31	43230	86.17	3-METHYL PENTANE
32	43223	70.14	3-METHYL-1-BUTENE
33	43211	84.16	3-METHYL-1-PENTENE
34	43270	84.16	3-METHYL-T-2-PENTENE
35	43298	114.23	3-METHYLHEPTANE
36	43295	100.20	3-METHYLHEXANE
37	43293	84.16	4-METHYL-T-2-PENTENE
38	43297	114.23	4-METHYLHEPTANE
39	45221	118.15	A-METHYLSTYRENE
40	43503	44.05	ACETALDEHYDE
41	43404	60.05	ACETIC ACID
42	43551	58.08	ACETONE
43	43702	41.05	ACETONITRILE
44	43206	26.04	ACETYLENE
45	43704	53.06	ACRYLONITRILE
46	45201	78.11	BENZENE
47	43213	56.10	BUTENE
48	43308	118.17	BUTYL CELLOSOLVE
49	43510	72.12	BUTYRALDEHYDE
50	43268	84.16	C-3-HEXENE

(continued)

TABLE B-3

SPECIES NO.	SAROAD CODE	MOLECULAR WEIGHT	CHEMICAL NAME
51	43115	98.19	C-7 CYCLOPARAFFINS
52	43116	112.23	C-8 CYCLOPARAFFINS
53	43117	126.26	C-9 CYCLOPARAFFINS
54	43511	58.08	C3 ALDEHYDE
55	43512	86.14	C5 ALDEHYDE
56	43289	84.16	C6 OLEFIN UNK
57	43294	98.18	C7-OLEFIN UNKNOWN
58	43513	128.21	C8 ALDEHYDE
59	43290	112.23	C8 OLEFIN UNK
60	43807	331.67	CARBON TETRABROMIDE
61	43804	153.84	CARBON TETRACHLORIDE
62	43311	90.12	CELLOSOLVE
63	43443	132.00	CELLOSOLVE ACETATE
64	43801	112.56	CHLOROBENZENE
65	43803	119.39	CHLOROFORM
66	43217	56.10	CIS-2-BUTENE
67	43227	70.13	CIS-2-PENTENE
68	43248	84.16	CYCLOHEXANE
69	43264	98.15	CYCLOHEXANONE
70	43273	82.14	CYCLOHEXENE
71	43242	70.14	CYCLOPENTANE
72	43292	68.11	CYCLOPENTENE
73	43207	42.08	CYCLOPROPANE
74	43320	116.16	DIACETONE ALCOHOL
75	43823	120.92	DICHLORODIFLUOROMETHANE
76	43802	84.94	DICHLOROMETHANE
77	45103	134.21	DIMETHYLETHYLBENZENE
78	43450	73.09	DIMETHYLFORMAMIDE
79	43287	310.59	DOCOSANE
80	43285	282.54	EICOSANE
81	43202	30.07	ETHANE
82	43433	88.10	ETHYL ACETATE
83	43438	100.11	ETHYL ACRYLATE
84	43302	46.07	ETHYL ALCOHOL
85	43812	64.52	ETHYL CHLORIDE
86	43351	74.12	ETHYL ETHER
87	43219	54.09	ETHYLACETYLENE
88	43721	45.09	ETHYLAMINE
89	45203	106.16	ETHYLBENZENE
90	43288	112.23	ETHYLCYCLOHEXANE
91	43203	28.05	ETHYLENE
92	43815	99.00	ETHYLENE DICHLORIDE
93	43370	62.07	ETHYLENE GLYCOL
94	43601	44.05	ETHYLENE OXIDE
95	43502	30.03	FORMALDEHYDE
96	43368	62.07	GLYCOL
97	43367	106.12	GLYCOL ETHER
98	43286	296.57	HENEICOSANE
99	43282	240.46	HEPTADECANE
100	43232	100.20	HEPTANE

(continued)

TABLE B-3

SPECIES NO.	SAROAD CODE	MOLECULAR WEIGHT	CHEMICAL NAME
101	43281	226.44	HEXADECANE
102	43231	86.17	HEXANE
103	43214	58.12	ISOBUTANE
104	43446	116.16	ISOBUTYL ACETATE
105	43306	74.12	ISOBUTYL ALCOHOL
106	43451	144.21	ISOBUTYL ISOBUTYRATE
107	43215	56.10	ISOBUTYLENE
108	43120	56.10	ISOMERS OF BUTENE
109	45105	134.21	ISOMERS OF BUTYLBENZENE
110	43109	142.28	ISOMERS OF DECANE
111	45106	134.21	ISOMERS OF DIETHYLBENZENE
112	43112	170.33	ISOMERS OF DODECANE
113	45104	120.19	ISOMERS OF ETHYLTOLUENE
114	43106	100.20	ISOMERS OF HEPTANE
115	43105	86.17	ISOMERS OF HEXANE
116	45234	134.21	ISOMERS OF METHYLPROP. BENZENE
117	43108	128.25	ISOMERS OF NONANE
118	43107	114.23	ISOMERS OF OCTANE
119	43114	212.41	ISOMERS OF PENTADECANE
120	43122	72.15	ISOMERS OF PENTANE
121	43121	70.13	ISOMERS OF PENTENE
122	45108	120.19	ISOMERS OF PROPYLBENZENE
123	43113	198.38	ISOMERS OF TETRADECANE
124	43111	184.36	ISOMERS OF TRIDECANE
125	45107	120.19	ISOMERS OF TRIMETHYLBENZENE
126	43110	156.30	ISOMERS OF UNDECANE
127	45102	106.16	ISOMERS OF XYLENE
128	43221	72.15	ISOPENTANE
129	43444	104.00	ISOPROPYL ACETATE
130	43304	60.09	ISOPROPYL ALCOHOL
131	43119	114.23	LACTOL SPIRITS
132	45212	120.19	M-ETHYLTOLUENE
133	45205	106.16	M-XYLENE
134	43201	16.04	METHANE
135	43432	74.08	METHYL ACETATE
136	43301	32.04	METHYL ALCOHOL
137	43445	140.00	METHYL AMYL ACETATE
138	43310	76.11	METHYL CELLOSOLVE
139	43801	50.49	METHYL CHLORIDE
140	43552	72.10	METHYL ETHYL KETONE
141	43560	100.16	METHYL ISOBUTYL KETONE
142	43559	100.16	METHYL N-BUTYL KETONE
143	43209	40.06	METHYLACETYLENE
144	43261	98.18	METHYLCYCLOHEXANE
145	43262	84.16	METHYLCYCLOPENTANE
146	43272	82.14	METHYLCYCLOPENTENE
147	43819	173.85	METHYLENE BROMIDE
148	43118	114.23	MINERAL SPIRITS
149	43212	58.12	N-BUTANE
150	43435	116.16	N-BUTYL ACETATE

(continued)

TABLE B-3

SPECIES NO.	SAROAD CODE	MOLECULAR WEIGHT	CHEMICAL NAME
151	43305	74.12	N-BUTYL ALCOHOL
152	43238	142.28	N-DECANE
153	43255	170.33	N-DODECANE
154	43260	212.41	N-PENTADECANE
155	43220	72.15	N-PENTANE
156	43303	60.09	N-PROPYL ALCOHOL
157	45209	120.19	N-PROPYLBENZENE
158	43259	198.38	N-TETRADECANE
159	43258	184.36	N-TRIDECANE
160	45101	114.23	NAPTHA
161	43284	268.51	NONADECANE
162	43235	128.25	NONANE
163	45211	120.19	O-ETHYLTOLUENE
164	45204	106.16	O-XYLENE
165	43283	254.49	OCTADECANE
166	43233	114.23	OCTANE
167	45206	106.16	P-XYLENE
168	43817	165.85	PERCHLOROETHYLENE
169	45300	94.11	PHENOLS
170	43265	40.06	PROPADIENE
171	43204	44.09	PROPANE
172	43504	58.08	PROPRIONALDEHYDE
173	43434	102.13	PROPYL ACETATE
174	43205	42.08	PROPYLENE
175	43369	76.00	PROPYLENE GLYCOL
176	43602	58.08	PROPYLENE OXIDE
177	43208	40.06	PROPYNE
178	45216	134.21	SEC-BUTYLBENZENE
179	45220	104.14	STYRENE
180	43123	136.24	TERPENES
181	43309	74.12	TERT-BUTYL ALCOHOL
182	45215	134.21	TERT-BUTYLBENZENE
183	43390	72.10	TETRAHYDROFURAN
184	45232	134.21	TETRAMETHYLBENZENE
185	45202	92.13	TOLUENE
186	43216	56.10	TRANS-2-BUTENE
187	43226	70.13	TRANS-2-PENTENE
188	45233	148.23	TRI/TETRAALKYL BENZENE
189	43824	131.40	TRICHLOROETHYLENE
190	43811	137.37	TRICHLOROFLUOROMETHANE
191	43821	187.38	TRICHLOROTRIFLUOROETHANE
192	43740	59.11	TRIMETHYL AMINE
193	43822	92.00	TRIMETHYLFLUOROSILANE
194	43241	156.30	UNDECANE
195	43000	86.00	UNKNOWN SPECIES
196	43860	62.50	VINYL CHLORIDE
197	45401	230.00	XYLENE BASE ACIDS

(concluded)

TABLE B-4. BOND GROUPS PER MOLECULE
(IN ALPHABETICAL ORDER)

SPECIES NO.	CHEMICAL NAME	SPECIES PROFILES BY BOND GROUP OLE	PAR	ARO	CARB	ETH	UNREACTIVE
1	1,1,1-TRICHLOROETHANE						2.00
2	1,1,2-TRICHLOROETHANE						2.00
3	1,1-DICHLOROETHANE						2.00
4	1,2,3-TRIMETHYLBENZENE		3.00	1.00			
5	1,2,4-TRIMETHYLBENZENE		3.00	1.00			
6	1,3,5-TRIMETHYLBENZENE		3.00	1.00			
7	1,3-BUTADIENE	1.00			2.00		
8	1,4-DIOXANE	1.00	2.00		2.00		
9	1-HEXENE	1.00	4.00				
10	1-PENTENE	1.00	3.00				
11	1-T-2-C-4-TM-CYCLOPENTANE		7.00		1.00		
12	2,2,3-TRIMETHYLPENTANE		6.00				
13	2,2,4-TRIMETHYLPENTANE		8.00				
14	2,2,5-TRIMETHYLPENTANE		8.00				
15	2,2-DIMETHYLBUTANE		6.00				
16	2,3,3-TRIMETHYLPENTANE		8.00				
17	2,3,4-TRIMETHYLPENTANE		8.00				
18	2,3-DIMETHYL-1-BUTENE	1.00	4.00				
19	2,3-DIMETHYLBUTANE		6.00				
20	2,3-DIMETHYLPENTANE		7.00				
21	2,4-DIMETHYLHEXANE		8.00				
22	2,4-DIMETHYLPENTANE		7.00				
23	2,5-DIMETHYLHEXANE		6.00				
24	2-ETHOXYETHYL ACETATE		4.00		2.00		
25	2-ETHYL-1-BUTENE	1.00	4.00				
26	2-METHYL PENTANE		6.00				
27	2-METHYL-1-BUTENE	1.00	3.00				
28	2-METHYL-2-BUTENE		3.00		2.00		
29	2-METHYL-2-PENTENE		4.00		2.00		
30	2-METHYLHEXANE		7.00				
31	3-METHYL PENTANE		6.00				
32	3-METHYL-1-BUTENE	1.00	3.00				
33	3-METHYL-1-PENTENE		6.00				
34	3-METHYL-T-2-PENTENE		4.00		2.00		
35	3-METHYLHEPTANE		8.00				
36	3-METHYLHEXANE		7.00				
37	4-METHYL-T-2-PENTENE		4.00		2.00		
38	4-METHYLHEPTANE		8.00				
39	A-METHYLSTYRENE		2.00	1.00	1.00		
40	ACETALDEHYDE		1.00		1.00		

(continued)

TABLE B-4

SPECIES PROFILES BY BOND GROUP

SPECIES NO.	CHEMICAL NAME	OLE	PAR	ARO	CARB	ETH	UNREACTIVE
41	ACETIC ACID		2.00				
42	ACETONE		2.00		1.00		
43	ACETONITRILE		1.00				1.00
44	ACETYLENE						1.00
45	ACRYLONITRILE	1.00	1.00				
46	BENZENE						6.00
47	BUTENE	1.00	2.00				
48	BUTYL CELLOSOLVE		5.00		1.00		
49	BUTYRALDEHYDE		3.00		1.00		
50	C-3-HEXENE	1.00	4.00				
51	C-7 CYCLOPARAFFINS		6.00		1.00		
52	C-8 CYCLOPARAFFINS		7.00		1.00		
53	C-9 CYCLOPARAFFINS		8.00		1.00		
54	C3 ALDEHYDE		2.00		1.00		
55	C5 ALDEHYDE		4.00		1.00		
56	C6 OLEFIN UNK	1.00	4.00				
57	C7-OLEFIN UNKNOWN	1.00	5.00				
58	C8 ALDEHYDE		7.00		1.00		
59	C8 OLEFIN UNK	1.00	6.00				
60	CARBON TETRABROMIDE						1.00
61	CARBON TETRACHLORIDE						1.00
62	CELLOSOLVE		3.00		1.00		
63	CELLOSOLVE ACETATE		4.00		2.00		
64	CHLOROBENZENE						6.00
65	CHLOROFORM						1.00
66	CIS-2-BUTENE		2.00		2.00		
67	CIS-2-PENTENE		3.00		2.00		
68	CYCLOHEXANE		5.00		1.00		
69	CYCLOHEXANONE		4.00		2.00		
70	CYCLOHEXENE	1.00	4.00				
71	CYCLOPENTANE		4.00		1.00		
72	CYCLOPENTENE	1.00	3.00				
73	CYCLOPROPANE		2.00		1.00		
74	DIACETONE ALCOHOL		5.00		1.00		
75	DICHLORODIFLUOROMETHANE						1.00
76	DICHLOROMETHANE						1.00
77	DIMETHYLETHYLBENZENE		4.00	1.00			
78	DIMETHYLFORMAMIDE						3.00
79	DOCOSANE		22.00				
80	EICOSANE		20.00				

(continued)

TABLE B-4

SPECIES PROFILES BY BOND GROUP

SPECIES NO.	CHEMICAL NAME	OLE	PAR	ARO	CARB	ETH	UNREACTIVE
81	ETHANE						2.00
82	ETHYL ACETATE		3.00		1.00		
83	ETHYL ACRYLATE		3.00		2.00		
84	ETHYL ALCOHOL		2.00				2.00
85	ETHYL CHLORIDE				1.00		
86	ETHYL ETHER		3.00				1.00
87	ETHYLACETYLENE		4.00				
88	ETHYLAMINE		1.00				
89	ETHYLBENZENE		2.00	1.00			
90	ETHYLCYCLOHEXANE		7.00		1.00		
91	ETHYLENE					1.00	
92	ETHYLENE DICHLORIDE					1.00	
93	ETHYLENE GLYCOL		1.00		1.00		
94	ETHYLENE OXIDE		1.00				1.00
95	FORMALDEHYDE				1.00		
96	GLYCOL		1.00		1.00		
97	GLYCOL ETHER		1.00		1.00		
98	HENEICOSANE		21.00				
99	HEPTADECANE		17.00				
100	HEPTANE		7.00				
101	HEXADECANE		16.00				
102	HEXANE		6.00				
103	ISOBUTANE		4.00				
104	ISOBUTYL ACETATE		6.00				
105	ISOBUTYL ALCOHOL		4.00				
106	ISOBUTYL ISOBUTYRATE		7.00		1.00		
107	ISOBUTYLENE	1.00	2.00				
108	ISOMERS OF BUTENE		2.00		2.00		
109	ISOMERS OF BUTYLBENZENE		4.00	1.00			
110	ISOMERS OF DECANE		10.00				
111	ISOMERS OF DIETHYLBENZENE		4.00	1.00			
112	ISOMERS OF DODECANE		12.00				
113	ISOMERS OF ETHYLTOLUENE		3.00	1.00			
114	ISOMERS OF HEPTANE		7.00				
115	ISOMERS OF HEXANE		6.00				
116	ISOMERS OF METHYLPROP. BENZENE		4.00	1.00			
117	ISOMERS OF NONANE		9.00				
118	ISOMERS OF OCTANE		8.00				
119	ISOMERS OF PENTADECANE		15.00				
120	ISOMERS OF PENTANE ..		5.00				

(continued)

TABLE B-4

SPECIES PROFILES BY BOND GROUP

SPECIES NO.	CHEMICAL NAME	OLE	PAR	ARO	CARB	ETH	UNREACTIVE
121	ISOMERS OF PENTENE		3.00		2.00		
122	ISOMERS OF PROPYLBENZENE		3.00	1.00			
123	ISOMERS OF TETRADECANE		14.00				
124	ISOMERS OF TRIDECANE		13.00				
125	ISOMERS OF TRIMETHYLBENZENE		3.00	1.00			
126	ISOMERS OF UNDECANE		11.00				
127	ISOMERS OF XYLENE		2.00	1.00			
128	ISOPENTANE		5.00				
129	ISOPROPYL ACETATE		5.00				
130	ISOPROPYL ALCOHOL		3.00				
131	LACTOL SPIRITS		8.00				
132	M-ETHYLTOLUENE		3.00	1.00			
133	M-XYLENE		2.00	1.00			
134	METHANE						1.00
135	METHYL ACETATE						3.00
136	METHYL ALCOHOL		1.00				
137	METHYL AMYL ACETATE		8.00				
138	METHYL CELLOSOLVE		2.00		1.00		
139	METHYL CHLORIDE						
140	METHYL ETHYL KETONE		3.00		1.00		
141	METHYL ISOBUTYL KETONE		5.00		1.00		
142	METHYL N-BUTYL KETONE		5.00		1.00		
143	METHYLACETYLENE		1.50				1.50
144	METHYLCYCLOHEXANE		6.00		1.00		
145	METHYLCYCLOPENTANE		5.00		1.00		
146	METHYLCYCLOPENTENE	1.00	4.00				
147	METHYLENE BROMIDE						1.00
148	MINERAL SPIRITS		7.00		1.00		
149	N-BUTANE		4.00				
150	N-BUTYL ACETATE		5.00		1.00		
151	N-BUTYL ALCOHOL		4.00				
152	N-DECANE		10.00				
153	N-DODECANE		12.00				
154	N-PENTADECANE						
155	N-PENTANE		5.00				
156	N-PROPYL ALCOHOL		3.00				
157	N-PROPYLBENZENE		3.00	1.00			
158	N-TETRADECANE		14.00				
159	N-TRIDECANE						
160	NAPTHA		8.00				

(Continued)

TABLE B-4

SPECIES PROFILES BY BOND GROUP

SPECIES NO.	CHEMICAL NAME	OLE	PAR	ARO	CARB	ETH	UNREACTIVE
161	NONADECANE		19.00				
162	NONANE		9.00				
163	O-ETHYLTOLUENE		3.00	1.00			
164	O-XYLENE		2.00	1.00			
165	OCTADECANE		18.00				
166	OCTANE		8.00				
167	P-XYLENE		2.00	1.00			
168	PERCHLOROETHYLENE						2.00
169	PHENOLS						6.00
170	PROPADIENE		1.00		2.00		
171	PROPANE		1.50				1.50
172	PROPRIONALDEHYDE		2.00		1.00		
173	PROPYL ACETATE		4.00		1.00		
174	PROPYLENE	1.00	1.00				
175	PROPYLENE GLYCOL		2.00		1.00		
176	PROPYLENE OXIDE		2.00				1.00
177	PROPYNE		2.00				1.00
178	SEC-BUTYLBENZENE		4.00	1.00			
179	STYRENE		1.00	1.00	1.00		
180	TERPENES	1.00	8.00				
181	TERT-BUTYL ALCOHOL		3.00		1.00		
182	TERT-BUTYLBENZENE		4.00	1.00			
183	TETRAHYDROFURAN		3.00		1.00		
184	TETRAMETHYLBENZENE		4.00	1.00			
185	TOLUENE		1.00	1.00			
186	TRANS-2-BUTENE		2.00		2.00		
187	TRANS-2-PENTENE		3.00		2.00		
188	TRI/TETRAALKYL BENZENE		5.00	1.00			
189	TRICHLOROETHYLENE					1.00	
190	TRICHLOROFLUOROMETHANE						1.00
191	TRICHLOROTRIFLUOROETHANE						2.00
192	TRIMETHYL AMINE		3.00				
193	TRIMETHYLFLUOROSILANE						3.00
194	UNDECANE		11.00				
195	UNKNOWN SPECIES	0.10	4.00	0.25	0.32	0.16	
196	VINYL CHLORIDE					1.00	
197	XYLENE BASE ACIDS		2.00	1.00			

(concluded)